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ADDITIVE CONVERTER STUDIES

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by

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FORWARD

This report was prepared by Thermo Electron Engineering Corporation, Waltham, Massachusetts, on Air Force Contract AF33(657)-10130, under Task No. 817305 of Project No. 8173. The work was administered under the direction of Air Force Aero Propulsion Laboratory, Research and Technology Division. Mr. A. E. Wallis was Project Engineer for the Laboratory.

The studies reported herein began in November 1962, and were concluded in November 1963 and were performed by the Research Department of Thermo Electron Engineering Corporation under the technical direction of S. S. Kitrilakis, Research Manager. Mr. A. L. Hyland was responsible for the laboratory work during the first half of the program and Mr. L. vanSomeren was in charge of the corrosion tests and metallurgical examinations.

This report is the final report and it concludes the work on Contract No. AF33(657)-10130. The contract report number is 35-64.

ABSTRACT

Results of a program aimed at improving the performance of thermionic converters, through the use of cesium halide additives, are reported. These results show that such improvement is achieved and is due to the reduction of collector work function at each operating condition.

The reduction in work function is achieved by a shift in the ratio of collector-to-cesium reservoir temperature ratio at which the minimum collector work function is obtained, thus allowing the converter to be operated closer to the condition of minimum collector work function than is useful in the cesium-only case.

It is also reported that corrosion and metallurgical examinations show no evidence of chemical attack upon converter components, which can be attributed to the additives.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

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SECTION I
INTRODUCTION

The thermionic converter has shown considerable promise as a means of energy conversion. In fact, for certain applications it appears to be the only feasible means of conversion. The usefulness of the process can be increased, however, if the emitter temperatures can be lowered and the conversion efficiencies increased. This was the aim of this one year program undertaken by Thermo Electron and sponsored by the Flight Vehicle Power Branch, USAF.

The approach taken was based on the experiments of several workers in the field who reported an enhancement of thermionic emission in the presence of cesium vapor and compounds of cesium with electro-negative elements. Langmuir¹ observed this with cesium oxide, Aamodt² reported on the effects of cesium fluoride, and more recently Jester³ reported also on cesium fluoride.

Specifically, the program was aimed at experimentally determining whether the lowering of the electrode work function in the presence of cesium halides could be achieved in an actual thermionic converter and whether it would result in an increase in performance for a given emitter temperature. The question of whether this effect was permanent or transient had to be answered and the corrosive effects, if any, of the additives on converter components were to be evaluated.

The experimental program consisted of two general categories of experiments:

1. Parametric performance testing to evaluate the effects of the presence of additives on converter performance.

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2. Life tests at operating temperature of converters charged with cesium and additives followed by metallurgical examination, to determine if any high rate of attack upon converter components is likely.

SECTION II

SUMMARY

1. This program has demonstrated that cesium halide additives when added to a cesium converter with refractory metal electrodes, will improve the performance of the thermionic converter. It has been shown that the improvement is the result of the reduction of the collector work function for the particular operating condition and that this reduction is achieved by a shift in the ratio of collector to cesium reservoir temperature at which the minimum collector work function is obtained. The shift allows the converter to be operated closer to the minimum collector work function condition than would be possible in the cesium only case.
2. Corrosion tests and metallurgical examinations have resulted in no evidence of chemical reactions that can be attributed to the presence of the additives. Photomicrographs show that all converter components examined after these tests were typical of such components exposed to cesium vapor only.
3. Converter performance appears to be independent of the additive reservoir temperature once a certain threshold temperature is exceeded, which should make possible the omission of the additive reservoir by locating the solid additive near the collector and providing an orifice at the inlet of the tube leading to the cesium reservoir.
4. An initial time lag of several hours is noted in realizing the effects of the additive.
5. Further experimental and analytical work is required to fully understand the phenomena noted in items 3 and 4 above and to determine the most useful manner of incorporating and controlling the additives to fully optimize its benefits to converter performance.

SECTION III

TEST VEHICLE

The experimental work on this program was conducted primarily on a thermionic converter test vehicle which had been designed prior to the time the program was initiated. At the start of the program, the design was slightly modified in order that the vehicle might accommodate the additive reservoir required for these experiments. The cross section of the modified converter is shown in Figure III-1. The emitter and collector are of plain parallel geometry and have an area of 3 cm^2 . The emitter (3) is supported with a thin walled member which connects to the emitter supporting structure and radiator (1). The collector and emitter structures are joined with a flexible seal (5) which allows variation of the spacing. The collector (4) is supported on a cylindrical member (6) which joins the main converter to its supporting structure. The emitter is heated by electron bombardment from an electron gun housed in the cavity behind the emitter. The emitter temperature is read in a blackbody hole on the backside of the emitter slab. The collector is also provided with a cavity which houses a heating filament, thus allowing the collector to be heated at any time during the operation of the converter. The collector temperature is maintained at a desired value by balancing the addition of heat from the resistance heater (9) against the heat withdrawn by a water cooling coil (11). The tubulation (8) connects the converter to the additive reservoir (10). The additive capsule (12) is contained in a closed tube below this reservoir and another tubulation connects the cesium reservoir (13) to the side of the additive reservoir. An orifice (15) is located at the opening of the cesium tubulation and allows the cesium pressure to be determined by the temperature of the cesium reservoir (13) while the additive pressure is determined by the temperature of its own reservoir. The vapor pressure of all the additives considered in this program is significantly lower than that of the cesium. It is,

therefore, necessary to operate the additive reservoir at considerably higher temperatures than the cesium reservoir, although the additive pressure is still significantly lower than the cesium pressure. The small aperture (15) allows the cesium vapor to be in equilibrium across it, while the additive passes through the orifice at an extremely low rate.

Figure III-2 is a photograph of the converter substructures before final assembly and Figure III-3 shows the converter after assembly is complete. The test vehicle proved sufficiently flexible for all of the experiments conducted during this program. The corrosion tests were performed in a simplified version of a hardware converter, shown in Figure III-4. This device employs all the materials typically used in thermionic converters, including the insulating seal. However, its simple design makes it quite inexpensive compared with the vehicle used for the performance tests.

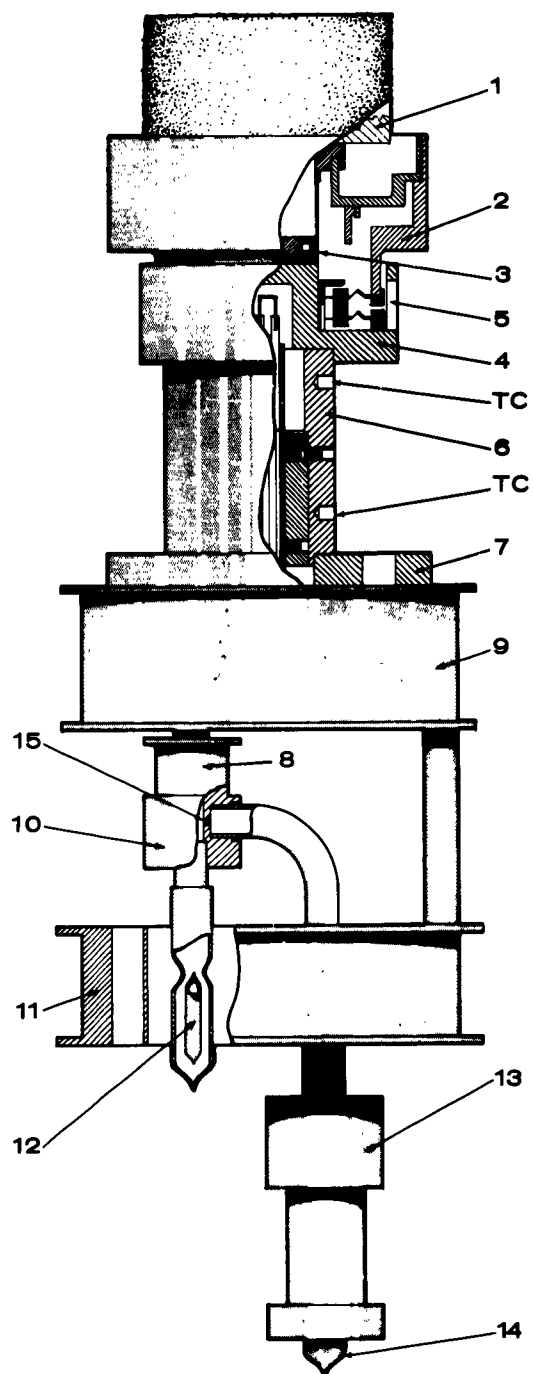


Figure III-1

Cross Section of Test Converter



Figure III-2 Photograph of Disassembled Additive Thermionic Converter

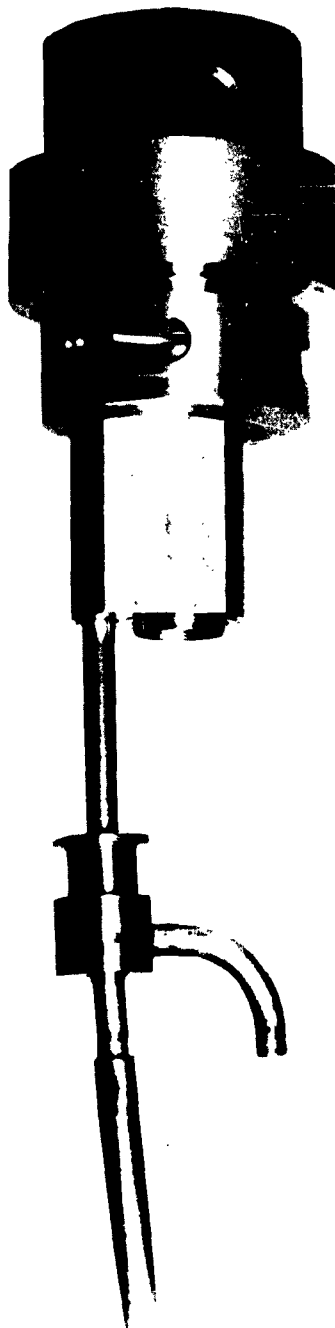


Figure III-3

Photograph of Additive Thermionic Converter

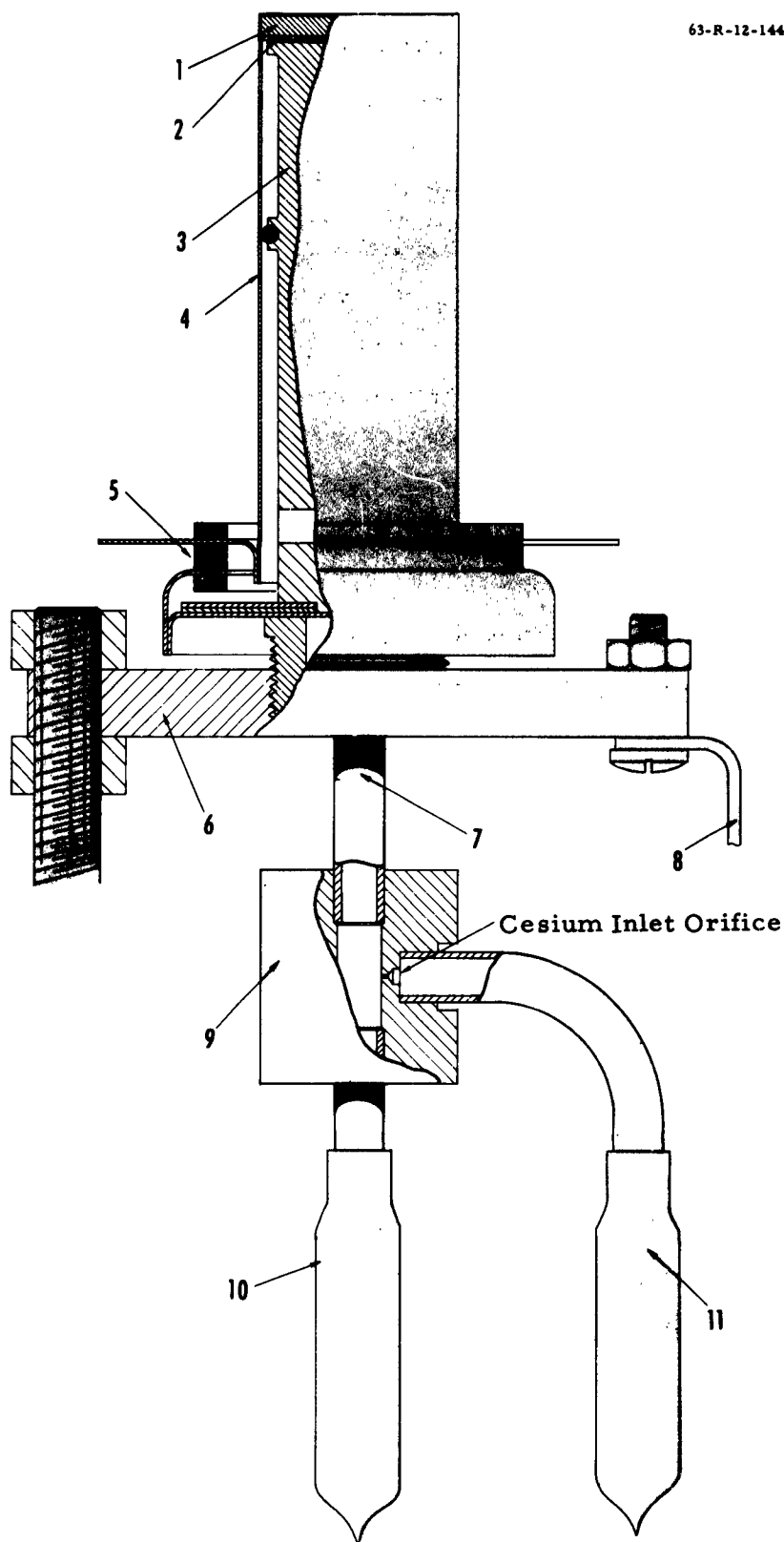


Figure III-4

Corrosion Test Vehicle

SECTION IV

EXPERIMENTAL RESULTS

A. Performance

This portion of the program consisted of taking comparative data on the performance of a cesium thermionic converter with and without the presence of additives. Both rhenium and tungsten were used as emitter materials opposite molybdenum collectors. Each emitter material was tested sufficiently, with cesium only in the converter, to establish that its performance conformed to the performance of the same material in previous parametric performance studies. This involved obtaining families of current voltage curves at several emitter temperatures and spacings. Subsequently, the metallic capsule containing the additive was broken and the additive was introduced into the converter. Testing of the converter was then continued with the additive reservoir temperature as a variable.

Figure IV-7 shows a typical family of current voltage curves for the cesium only condition. The individual current voltage curves cross each other and each curve exhibits a maximum current value at a specific voltage. This fact makes it possible to determine an envelope which is tangent to each current voltage curve and represents the maximum performance obtainable at the particular emitter temperature, spacing, and collector temperature employed. In comparing the performance of either the same material in two different converters, or different materials, it is far less ambiguous to compare these envelopes than to compare individual current voltage curves since a small variation in cesium reservoir temperature can result in a significant change in output voltage or saturation current. This method of comparison was used throughout the program being reported here. Figure IV-3 is a family taken at conditions very similar to those

of Figure IV-7 except that cesium fluoride was present. The effect of the cesium fluoride can immediately be appreciated by inspecting the two figures. The comparison between the two is emphasized by the superposition of the envelope of Figure IV-7 on Figure IV-3. The dotted line on Figure IV-3 represents the envelope from Figure IV-7.

Before discussing the experimental results obtained with each additive, certain general remarks should be made about the behavior of both additives. When the metal capsule containing the additive was opened, several hours were required before the effect of the additive was manifested as a change in performance. This behavior cannot be explained by the low vapor pressure of the additive, nor by any diffusion process through the cesium vapor. At this time, no satisfactory physical model has been devised to describe this process. It was observed, however, that once the effect of the additive becomes evident in the performance of the converter, lowering of the additive reservoir temperature does not reverse the process. In fact, the performance appears to be independent of additive reservoir temperature once this threshold is reached.

It may also be generally concluded that the primary effect of either of the additives appears to be a change in collector work function. The emitter work function remains relatively unaffected by any additive tried so far.

The performance of the tungsten emitter - molybdenum collector converter, charged with cesium plus cesium fluoride, is shown in Figure IV-1 through IV-6. The emitter temperatures range from 1540° K to 1950° K. A family of curves including approximately 10 current voltage characteristics, is shown in each figure. Each single characteristic is obtained as a specific cesium reservoir temperature, and an entire family covers a span in cesium reservoir temperature of between 70° and 100° K. Thus, each family includes the whole range of

parameter variation that is of interest from a power production standpoint. Figures IV-7 through IV-9 show families of current voltage curves taken before the cesium fluoride capsule was opened. The conditions of Figures IV-7, 8, and 9, correspond closely to those of Figures IV-3, 5, and 6, respectively. To facilitate comparison between these pairs of figures, the envelope for the cesium only family of curves is plotted as a dotted line on the figure showing the same family with the additive present. Inspection of any of the matched pairs of families will reveal that individual curves of approximately the same cesium reservoir temperature have saturation current values of nearly the same magnitude and that the shape of these curves is very similar. In fact, the two groups of curves can be superimposed by sliding them along the voltage axis. This, of course, is reflected in the fact that the envelopes of the curves are parallel to each other with the output voltages of the cesium-only envelope being smaller by about 0.1 volt.

A maximum power point can be determined for each of the envelopes described above. These maximum power points and the corresponding output voltage for the cesium-only case and for the cesium plus cesium fluoride case are shown in Figure IV-10. The data at 1540° K and 1590° K emitter temperature were taken at spacings of 15 mils while the remainder were obtained at 6 mils.

Figures IV-11, 12, and 13 summarize the performance of the rhenium emitter-molybdenum collector converter with cesium chloride additive. The corresponding families before the cesium chloride was introduced are shown in Figures IV-14, 15, and 16. For comparison, the envelopes of the families using only cesium are also plotted as dotted lines on Figures IV-11, 12, and 13. The effect of cesium chloride is seen to be very similar to that observed with the cesium fluoride in the tungsten - molybdenum converter. Figures IV-17, 18, 19, and 20 show envelopes of current voltage families for the rhenium emitter molybdenum collector

converter with and without cesium fluoride present. The data again show a translation of the envelope to higher voltages by about 0.1 volt when the additive was introduced.

A majority of the families of current voltage curves presented, were reproduced at least once during the testing program of each converter. The reproducibility was well within the experimental error known to exist in the measurement of the various parameters.

Several times the converters were allowed to reach equilibrium at a given set of conditions and then maintained at that point for a period of 10 to 20 hours. At the end of this time, the converter output was found to be very close to the value observed at the beginning of the test.

B. Collector Work Function

The performance data described above indicates that the only effect of the cesium halide additives is the translation of the current voltage curves. No other significant change has been observed within the experimental error of the measurements. This behavior suggests that a lowering of the collector work function has occurred due to the presence of the cesium halide additives. To verify this conclusion, a series of tests were conducted to determine the values of the collector work function. Prior to the initiation of the present program, the Research Department at Thermo Electron had obtained a correlation of the collector work function (in several molybdenum collector converters) with the ratio of collector temperature to reservoir temperature. This correlation proved to be unique and independent of any other parameters. Figure IV-36 shows this correlation for the cesium-only condition (curve A). The spread of the original experimental data was approximately 0.1 volt. The procedure used to obtain collector work function measurements consists of recording current voltage curves under ion rich condi-

tions by observing that the emitter saturation current increases for increasing cesium pressure and follows an exponential relationship with cesium pressure.

Figure IV-21 is a typical run. It will be observed that a backcurrent exists at high voltages; in fact, voltages higher than the open circuit. This backcurrent is presumably due to back emission ion currents and leakage across the emitter - collector insulator. When this backcurrent is added to the forward current, the resulting value of the current will correspond to the current modulated by the barrier created by the sum of the output voltage and collector work function. If this assumption is correct, the logarithm of the output current, corrected for the backcurrent, should be linearly dependent on output voltage and can be plotted upon semi-log paper as a straight line with a slope equal to $\frac{1}{kT_E}$. Figures IV-22 through IV-35 are such plots of data taken during this program.

The collector work function can be computed by substituting the emitter temperature and the output current density for the particular curve in the Richardson equation and then solving that equation for the corresponding barrier. This barrier is the sum of the output voltage and the collector work function and by subtracting from it the output voltage, the collector work function is determined. The results of these experiments are shown in Figure IV-36 as individual points. A curve (B) is passed through these points. The open circles correspond to the tungsten - molybdenum converter with cesium fluoride and the solid black circles correspond to the rhenium - molybdenum converter with cesium fluoride. Data points correlate within about 0.1 volt which is similar to the correlation obtained with the cesium-only converter shown in curve A of Figure IV-36. It is observed that the minimum work function obtained with the additives in the converter has not become any lower than it was when cesium-only was used. However, it has shifted to a lower value of collector temperature to cesium reservoir temperature (about 1.5 rather than 2).

The significance of the change of the value of $\frac{T_C}{T_R}$ at which the minimum work function occurs can be appreciated by realizing that the reservoir temperature is dictated by emission considerations. That is, for the emitter to yield a significant current at a given temperature, the cesium reservoir has to be confined within certain narrow limits. The collector work function correlation indicates that in the region of interest the collector work function drops with increasing values of collector to reservoir temperature ratio. To increase this ratio, with the reservoir temperature fixed, the collector temperature must be increased. Typical cesium reservoir temperatures required by the emitter are in the vicinity of 600° K. To achieve the minimum collector work function, for the cesium-only case, the ratio of $\frac{T_C}{T_R}$ must be approximately 2, and for a T_R equal to 600 T_C must then be equal to 1200. At 1200° C, however, back emission at the existing combination of electrode temperature and work function becomes very large, probably higher than the corresponding forward emission. This fact makes the minimum collector work function impossible to achieve for the cesium-only case. However, when the additive is present, it causes a shift of the value of $\frac{T_C}{T_R}$ at which the minimum collector work function occurs and the possibility of operating at the condition of minimum work function is achieved.

C. Corrosion Tests

In parallel with the experiments designed to determine the effect of compounds of cesium with electronegative elements on the performance of thermionic converters, tests were conducted aimed at detecting any corrosive effects of these compounds on converter structures.

The compounds considered in the program were CsF, CsCl, and Cs₂O. All three materials were obtained in purities 99.9% or higher, encapsulated in evacuated glass capsules. The glass capsules were broken and the salts quickly

transferred to metal capsules which were then outgassed at 150° C for 10 hours to expel any moisture adsorbed from the atmosphere before pinching off. These metal capsules were inserted in the test vehicles and broken at the appropriate time.

The above procedure proved satisfactory for CsCl and CsF but failed in the case of Cs₂O. The Cs₂O metal capsules when heated to 150° C during outgassing invariably leaked. The metal walls of the capsule were severely corroded in each case. It is not clear at this time what the mechanism of the chemical reaction taking place is, but after five trials, Cs₂O was abandoned in favor of testing a W emitter - Mo collector converter with CsF.

The metallurgical examinations described below were performed on test vehicle components exposed to Cs + CsF and Cs + CsCl at typical converter operating conditions for periods in excess of 350 hours for each additive salt.

The vehicle was mounted in plastic and sectioned. The sections were polished and, in some cases, etched locally with a swab.

Figure IV-37 shows the metal-ceramic seal, which is a critical part of the diode. Figure IV-38 is an enlargement of the extremity of the seal which was exposed to the inside of the diode. Each of these appears to be in good condition, and no significant corrosion is observed at the inner end. Figure IV-39 is of the Ni to Cu braze in the tubulation. The small crack at the interface at one edge of the picture is typical of this design of braze, in which the nickel tube is inserted in the copper tube, and heat applied locally to form a low melting Cu-Ni alloy. This process tends to leave a crack between the two tubes, which is not attributed to corrosion at the interface. Figure IV-40 shows the Ni-Mo braze. A copper base braze metal has alloyed considerably with the nickel tube and slightly with the

molybdenum. The extreme end of the nickel tube is tapered in toward the center during fabrication, and again the dark V between Ni and Mo is not attributed to corrosion.

Figures IV-41 and IV-42 show the inner (curved) surface of the Ni and Cu tubes, both of which are clean to the naked eye, and show some thermal etching of grain boundaries but no corrosion.

Figure IV-43 is of the face of the collector. This was found to have a small amount of black deposit on it when opened. This was easily wiped off before the photograph was taken; it is similar to deposits found in older diodes, which were then attributed to contamination of the cesium supplied to us. The collector surface of Mo, is typical of a hand lapped surface, and shows no significant changes since fabrication.

Figure IV-44 is of the Mo-Ni braze where it was exposed to the diode atmosphere. No corresponding photograph before exposure is available for comparison. There may be a small amount of corrosion at the free surface of the copper braze alloy, but this is doubtful. The Mo, Ni, and Cu separately, all have good corrosion resistance here, and the extent of the attack is extremely small. It has not begun to reach the structurally important part of the braze.

Figure IV-45 is the corresponding picture for the Mo-Ta braze. The above observations apply here too; there may possibly be a little corrosion, but it is not possible to confirm that there is any, and if there is, its extent is trivial.

Inspection of other parts of the diode with the naked eye and low power microscope revealed no significant corrosion. A few "spots" occurred and some small green deposits, possibly CuCl , were found, but in each case swabbing with water removed the deposit, and no localized pitting attack or grain boundary attack was

found. Experience on other corrosive systems suggests that all the corrosion observed here could reasonably be attributed to small traces of impurities in the metals present.

D. Conclusions

This examination gives no reason to believe that the presence of CsCl or CsF in the atmosphere of this would have shortened its life significantly by comparison with a like diode operating with cesium only.

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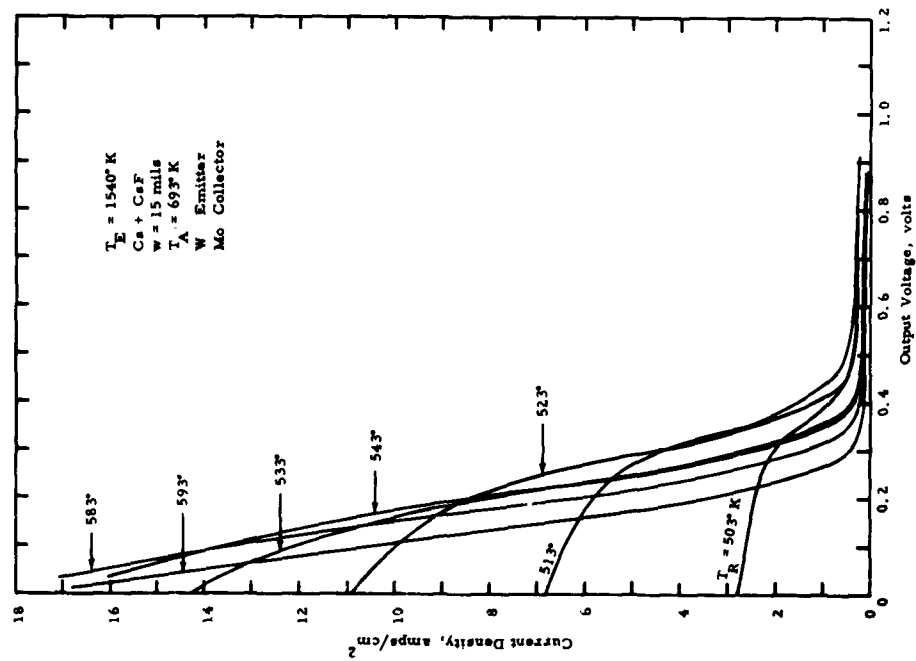


Figure IV-2 I-V Curve Family

63-R-12-146

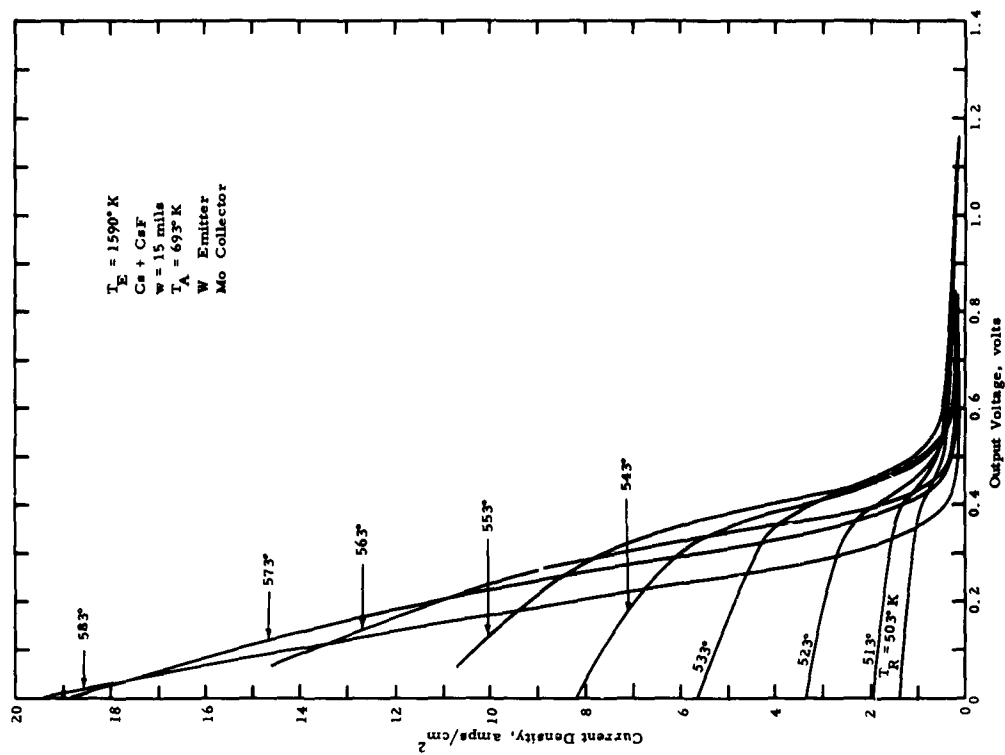


Figure IV-1 I-V Curve Family

63-R-12-147

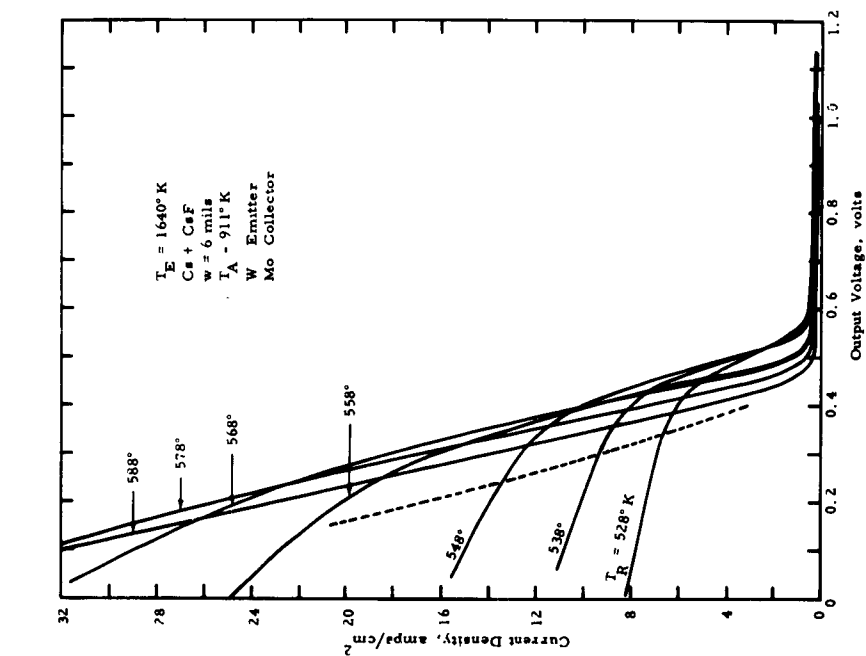


Figure IV-3 I-V Curve Family

63-R-12-148

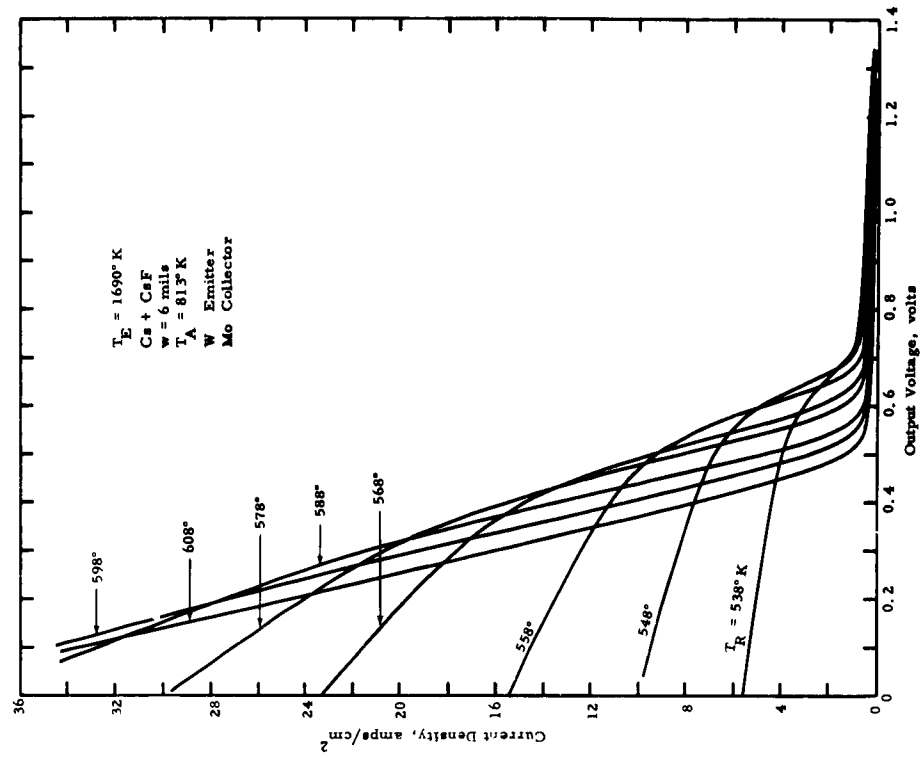


Figure IV-4 I-V Curve Family

63-R-12-149

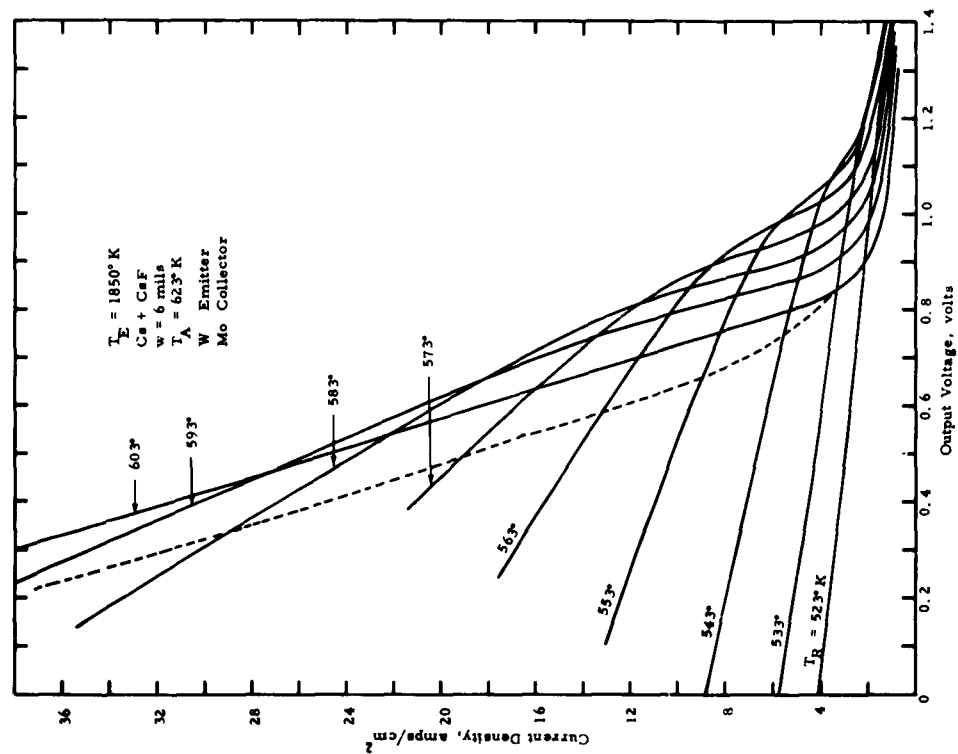


Figure IV-5 I-V Curve Family

63-R-12-150

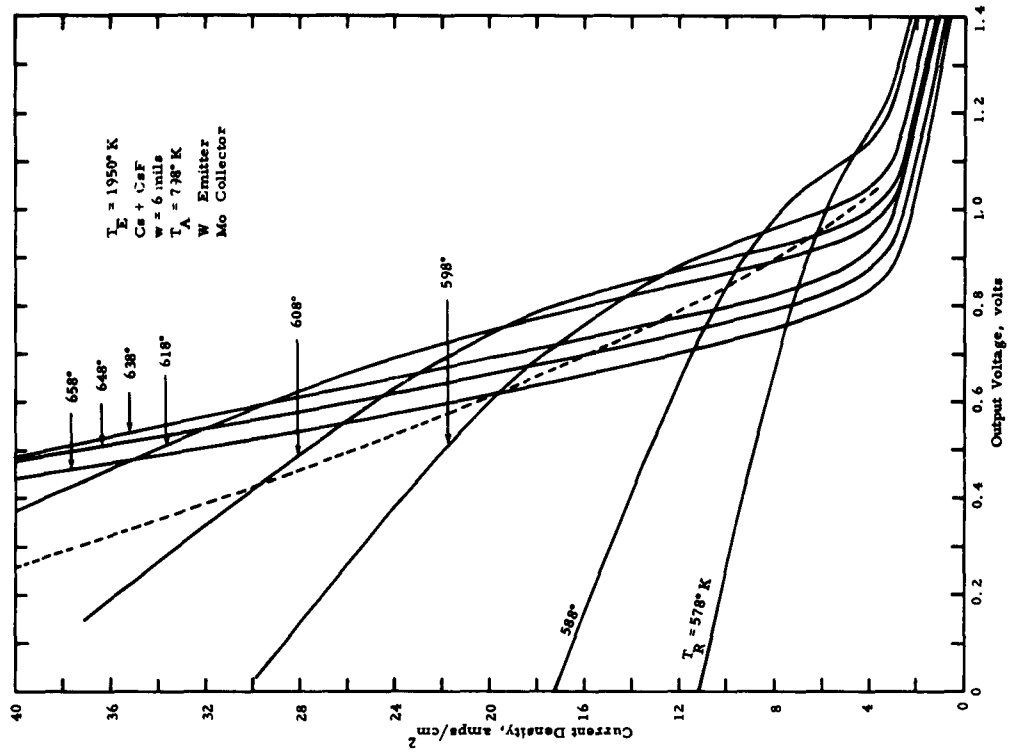


Figure IV-6 I-V Curve Family

63-R-12-151

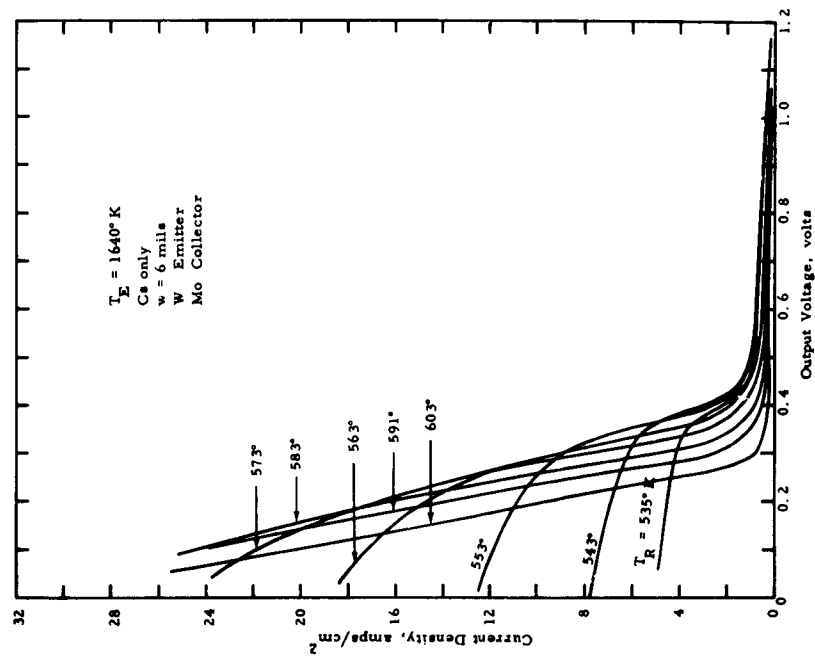


Figure IV-7 I-V Curve Family

63-R-12-152

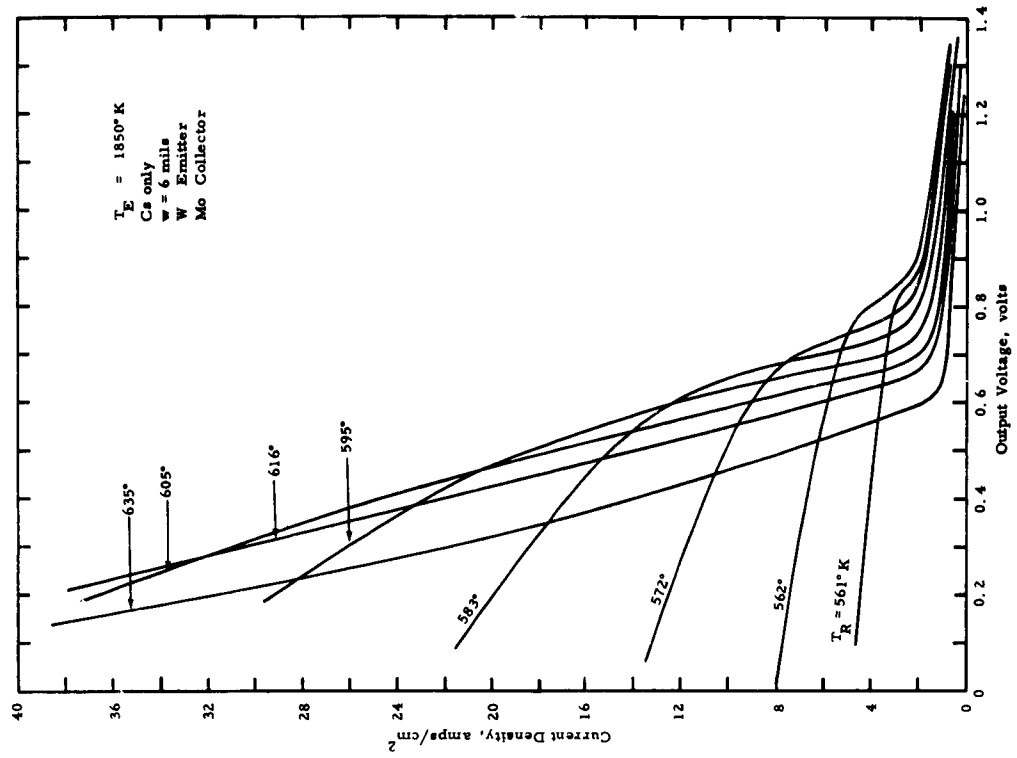


Figure IV-8 I-V Curve Family

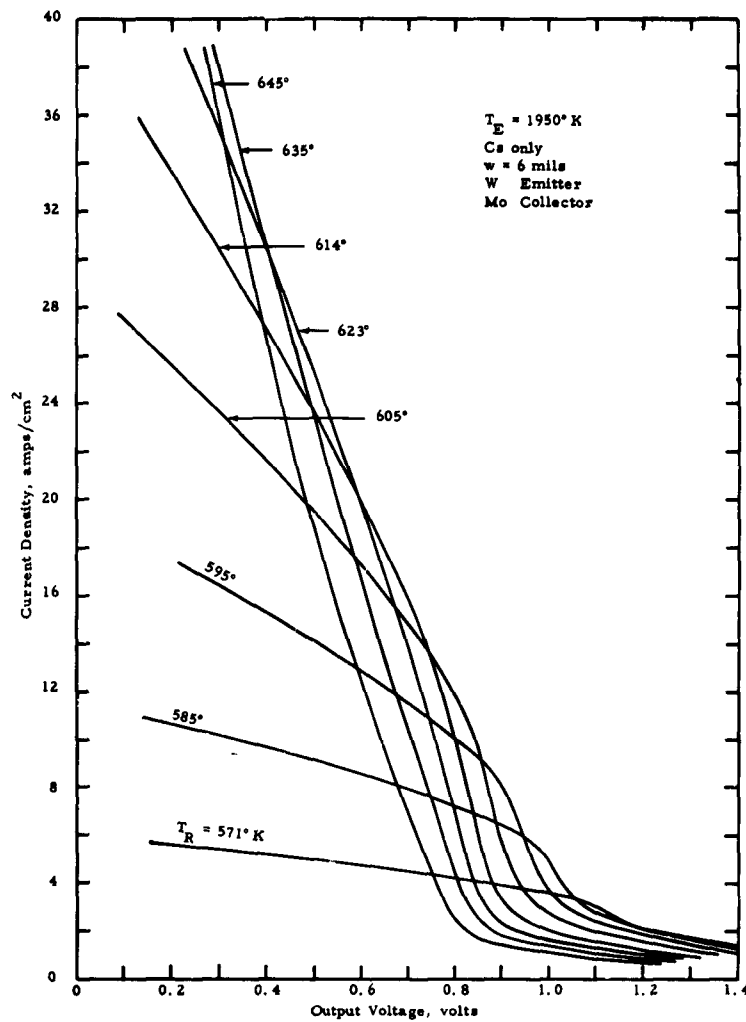


Figure IV-9 I-V Curve Family

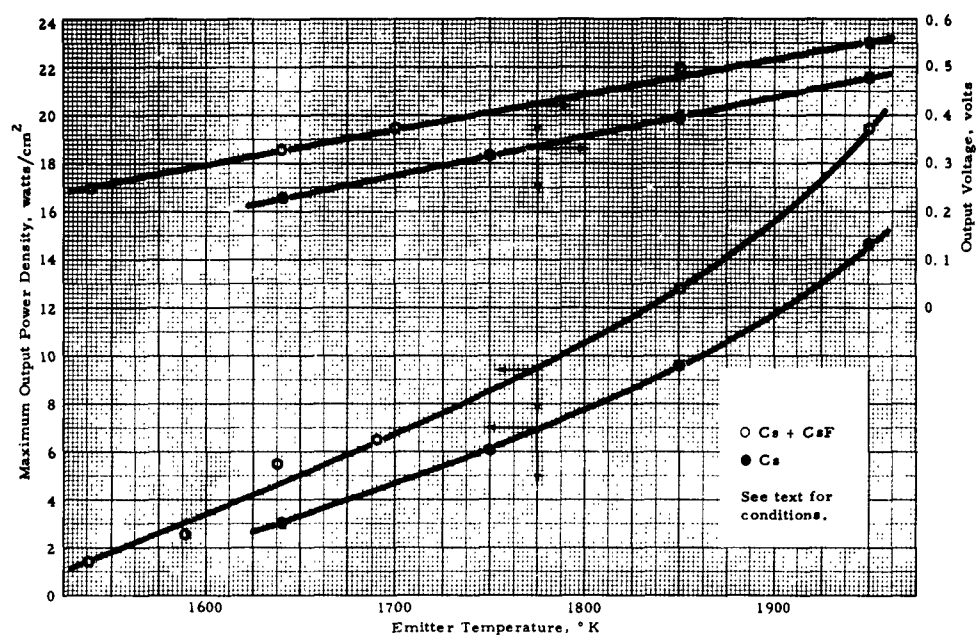


Figure IV-10 Maximum Power Points and Corresponding Output Voltages

63-R-12-155

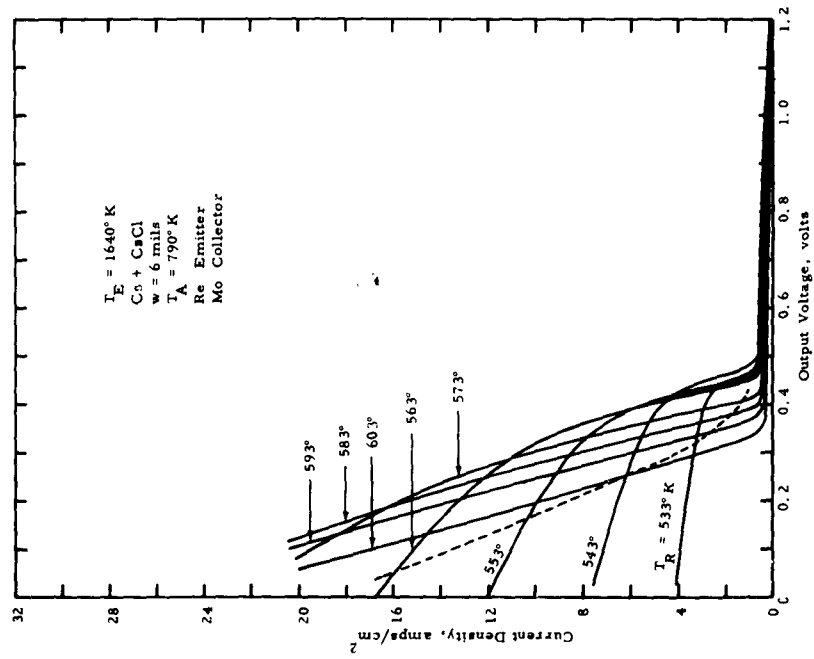


Figure IV-11 I-V Curve Family

63-R-12-156

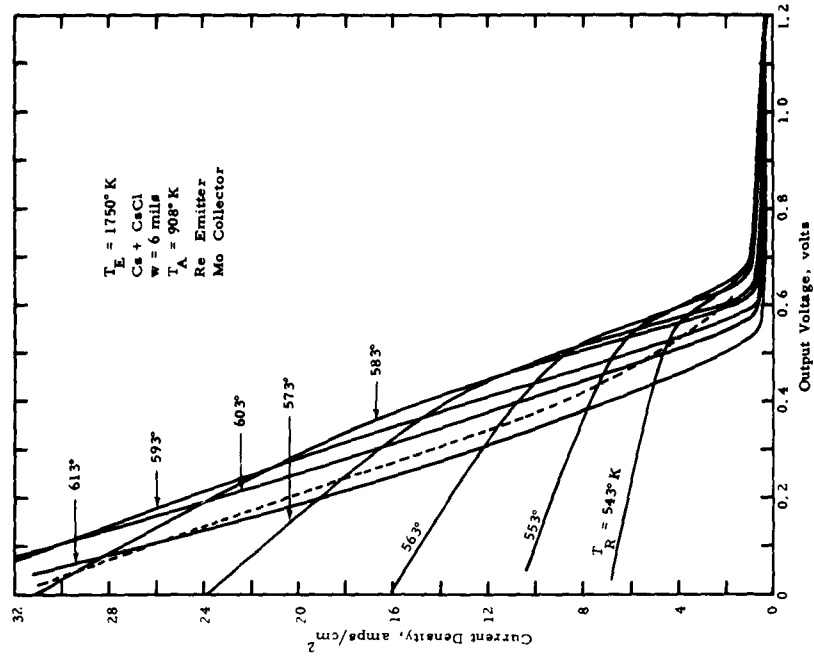


Figure IV-12 I-V Curve Family

63-R-12-157

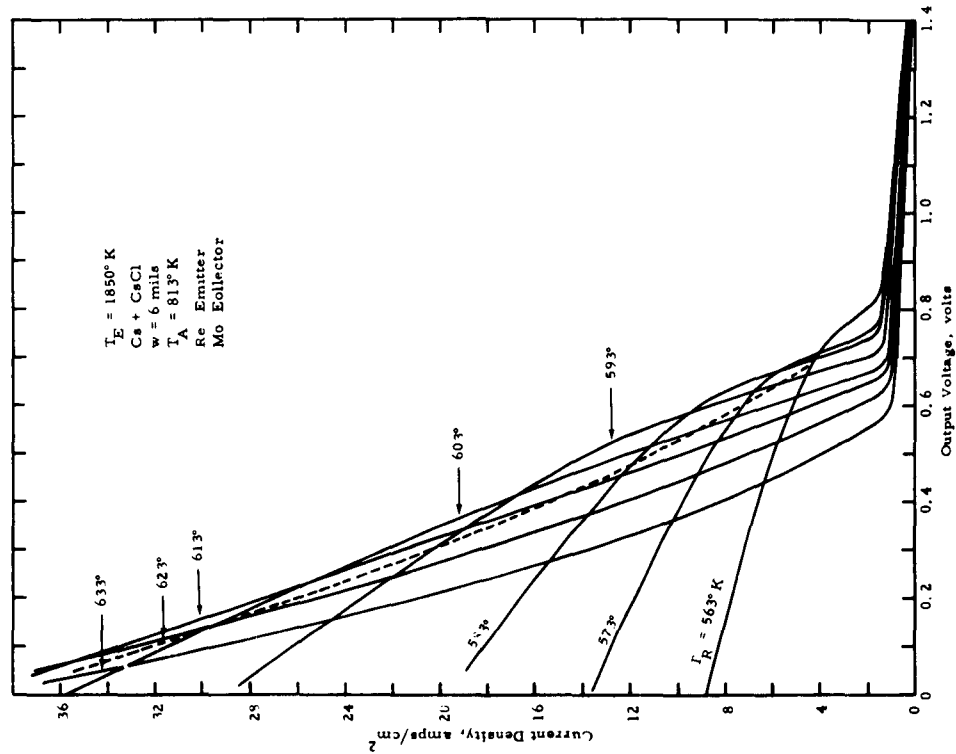


Figure IV-13 I-V Curve Family

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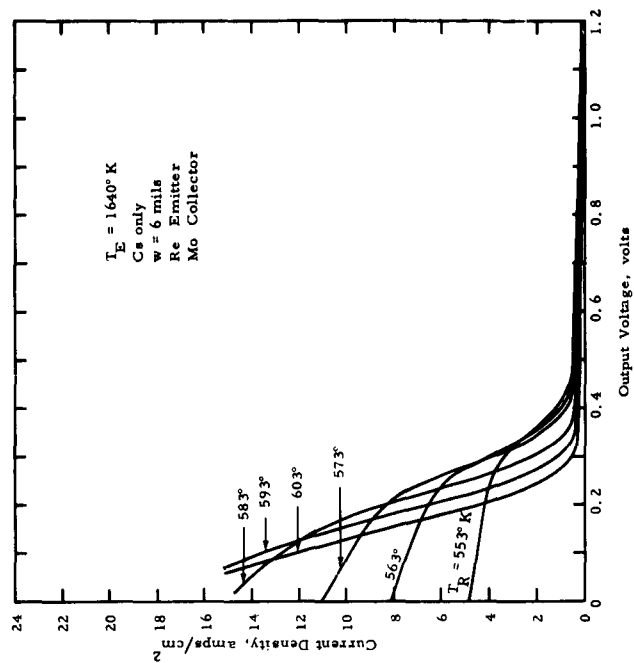


Figure IV-14 I-V Curve Family

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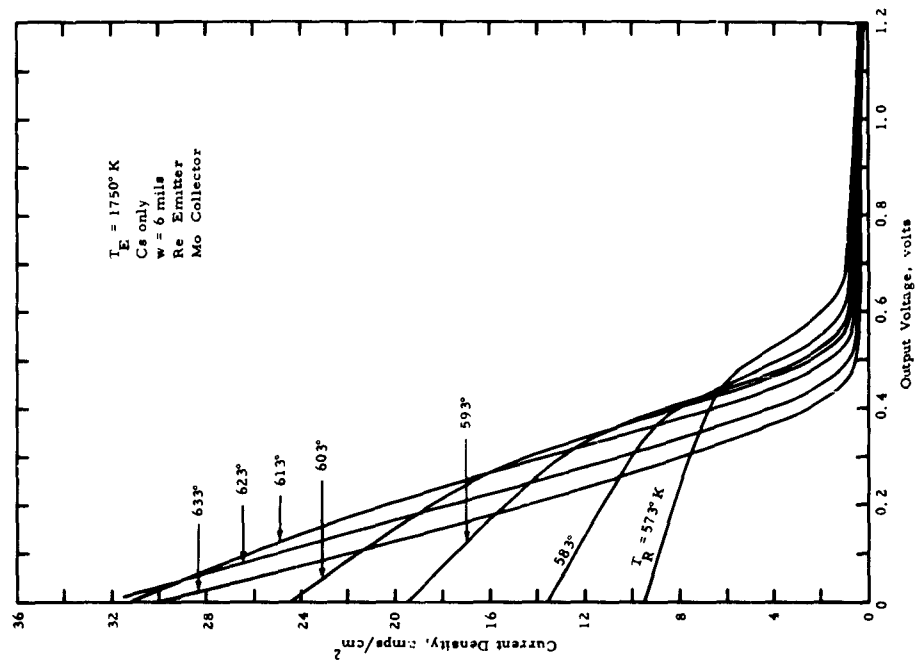


Figure IV-15 I-V Curve Family

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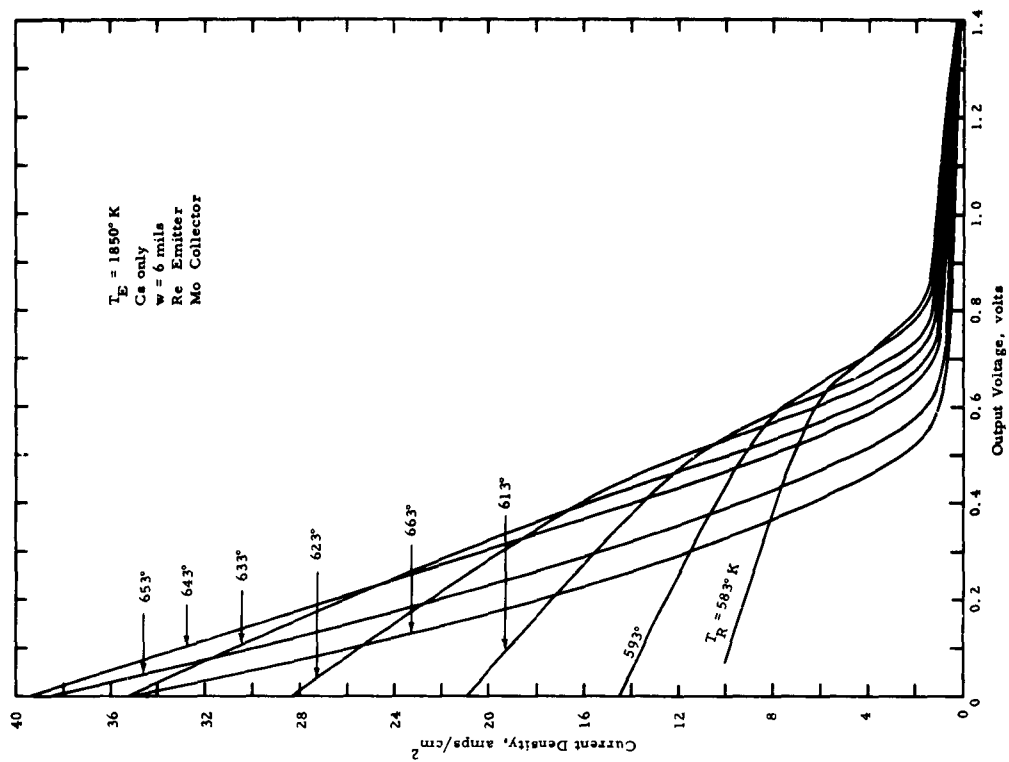


Figure IV-16 I-V Curve Family

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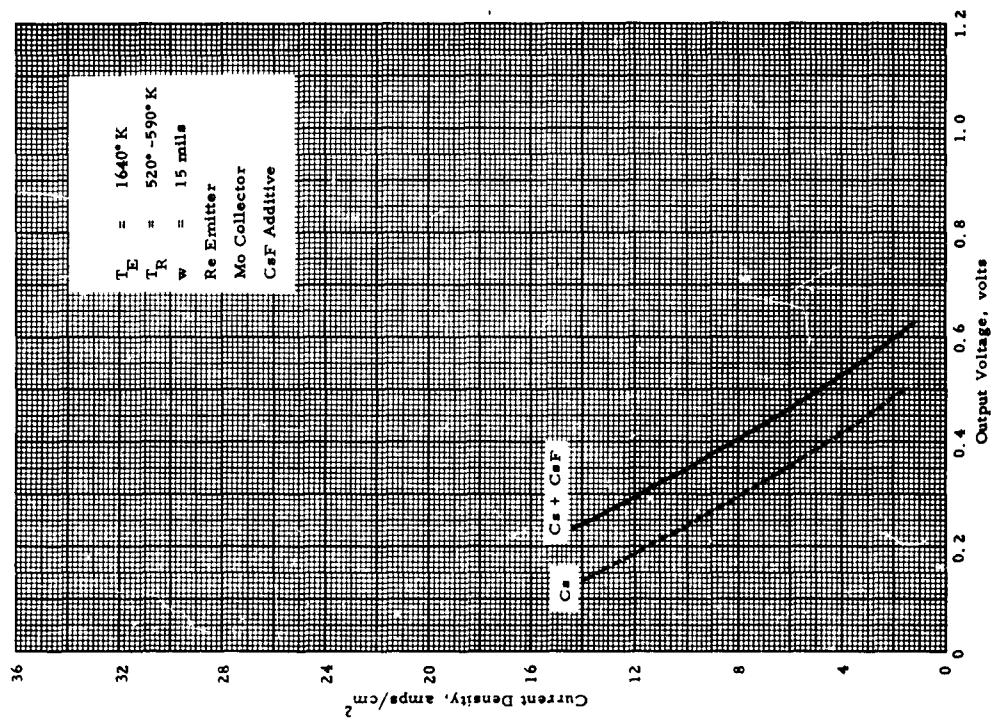


Figure IV-17 I-V Family Envelopes

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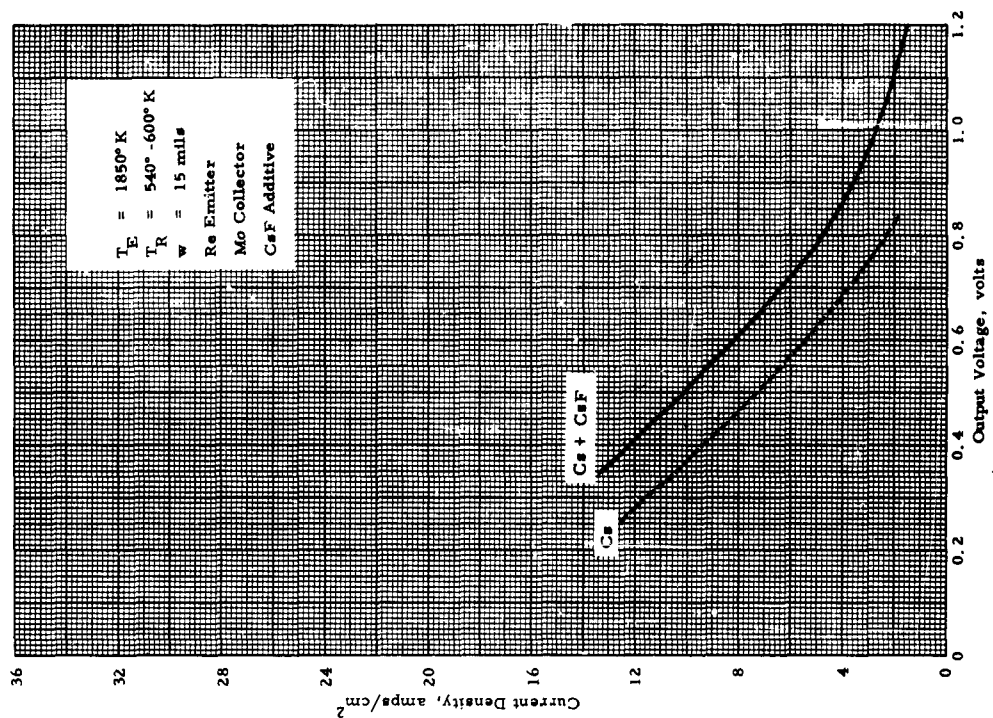


Figure IV-18 I-V Family Envelopes

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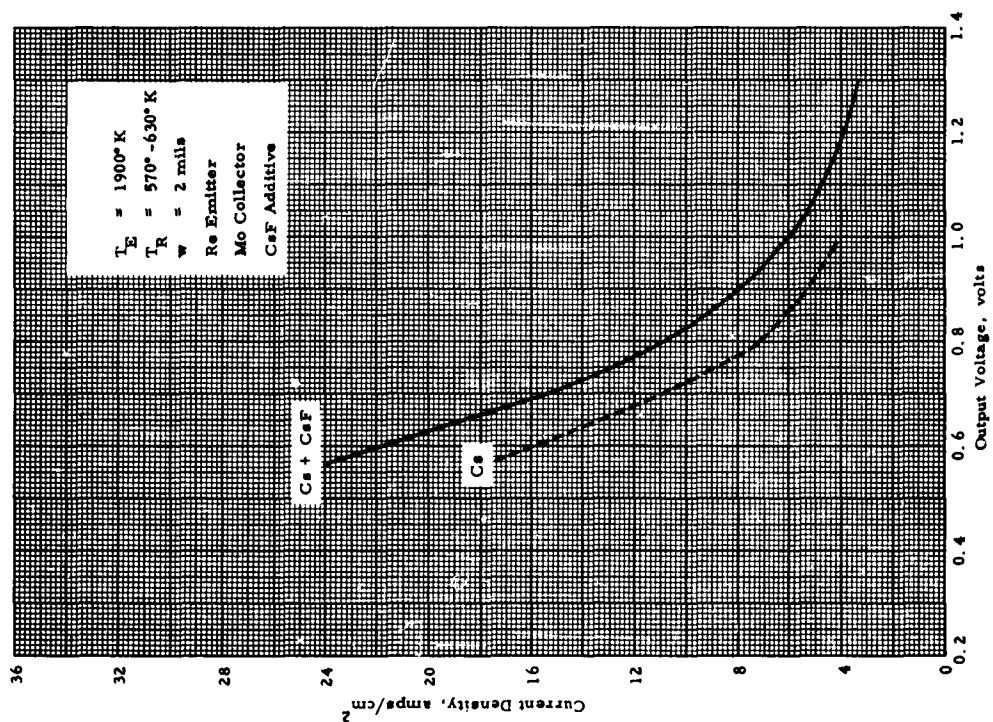


Figure IV-19 I-V Family Envelopes

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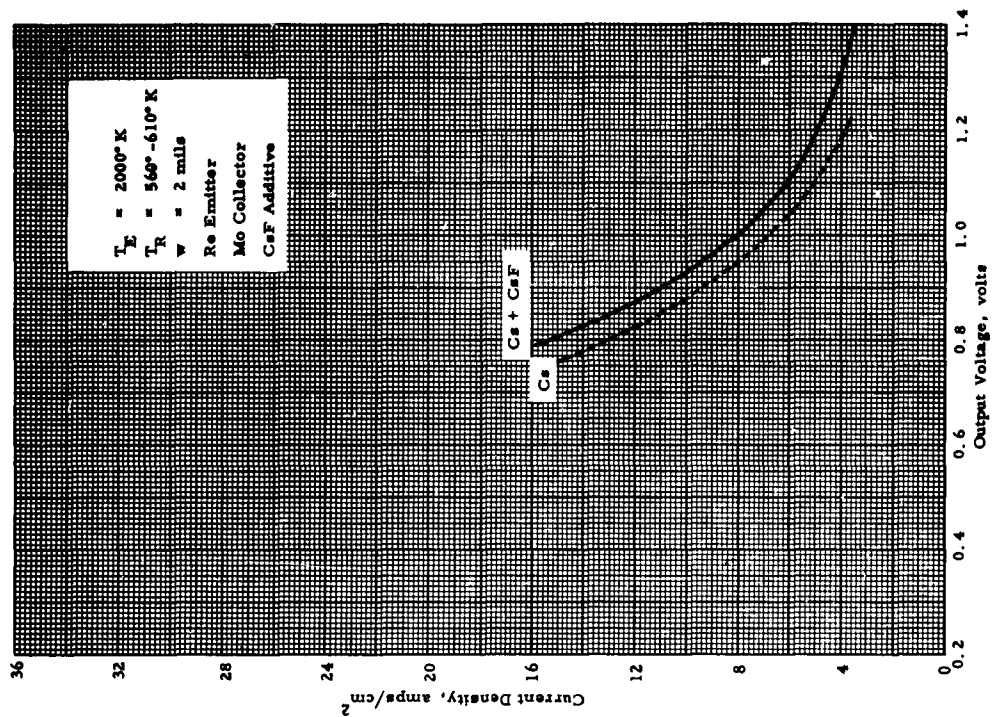


Figure IV-20 I-V Family Envelopes

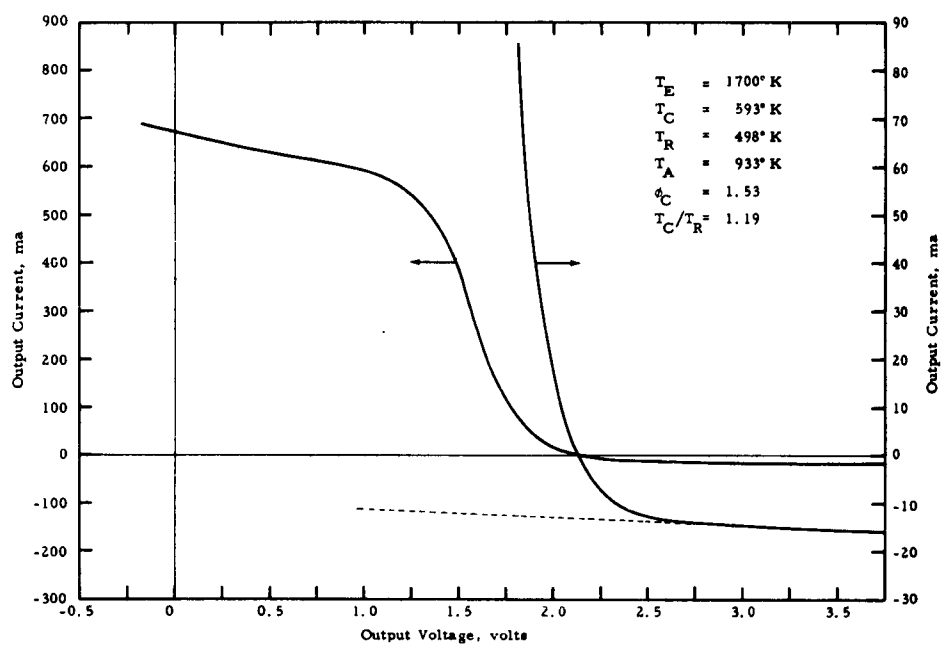


Figure IV-21 I-V Curve Used in Collector Work Function Determination

63-R-12-166

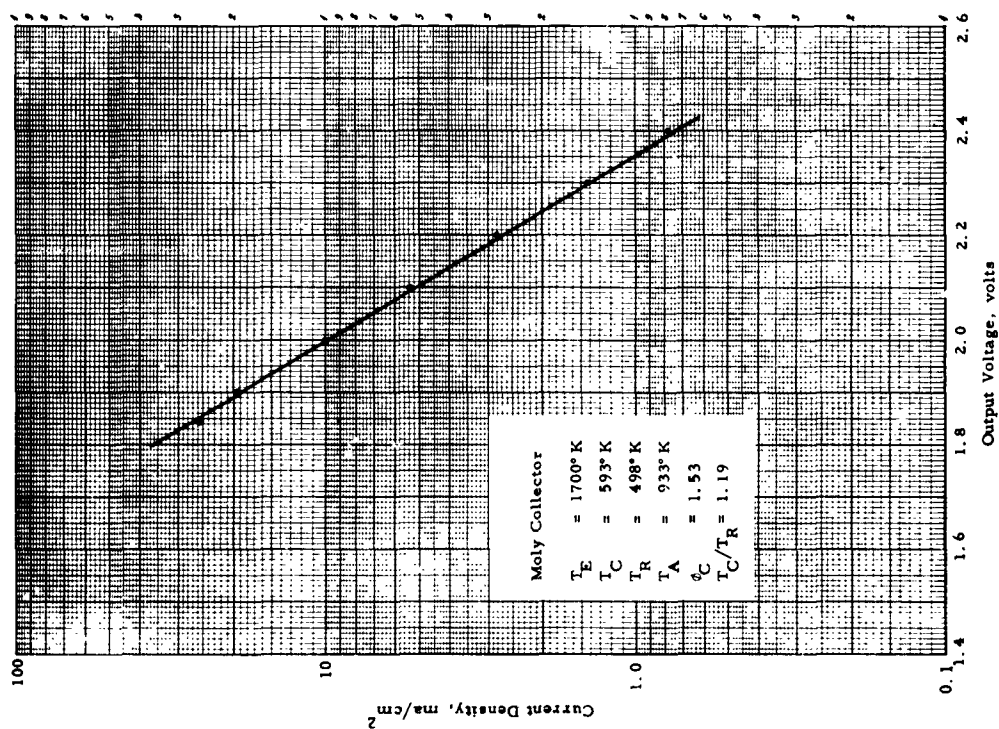


Figure IV-22 Semi-Log Plot

63-R-12-167

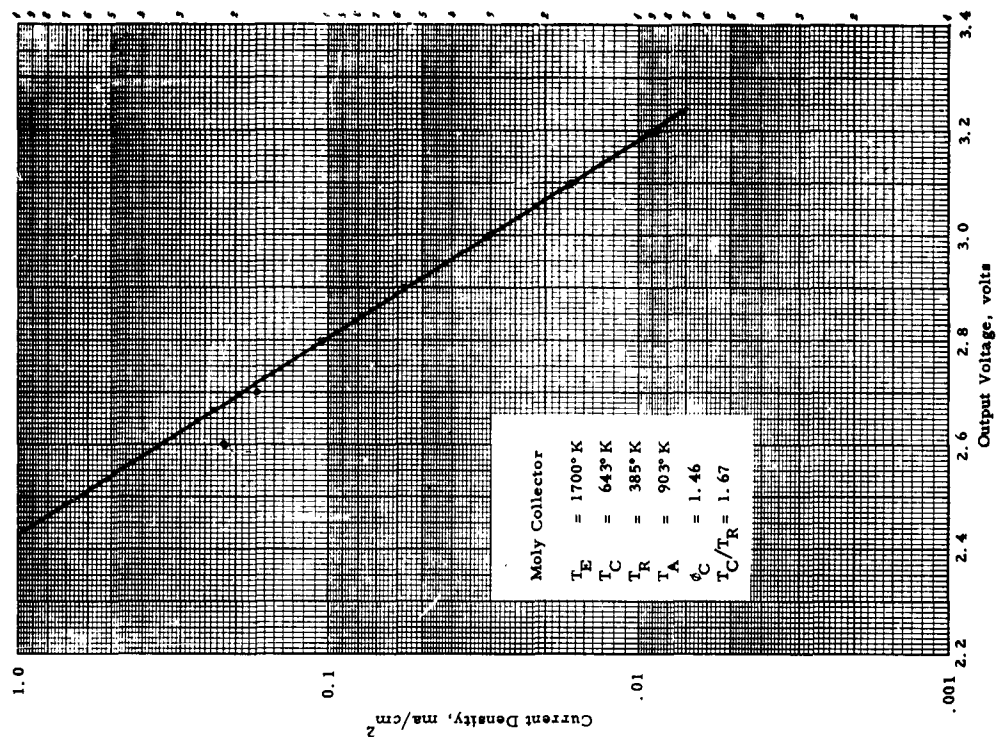


Figure IV-23 Semi-Log Plot

63-R-12-168

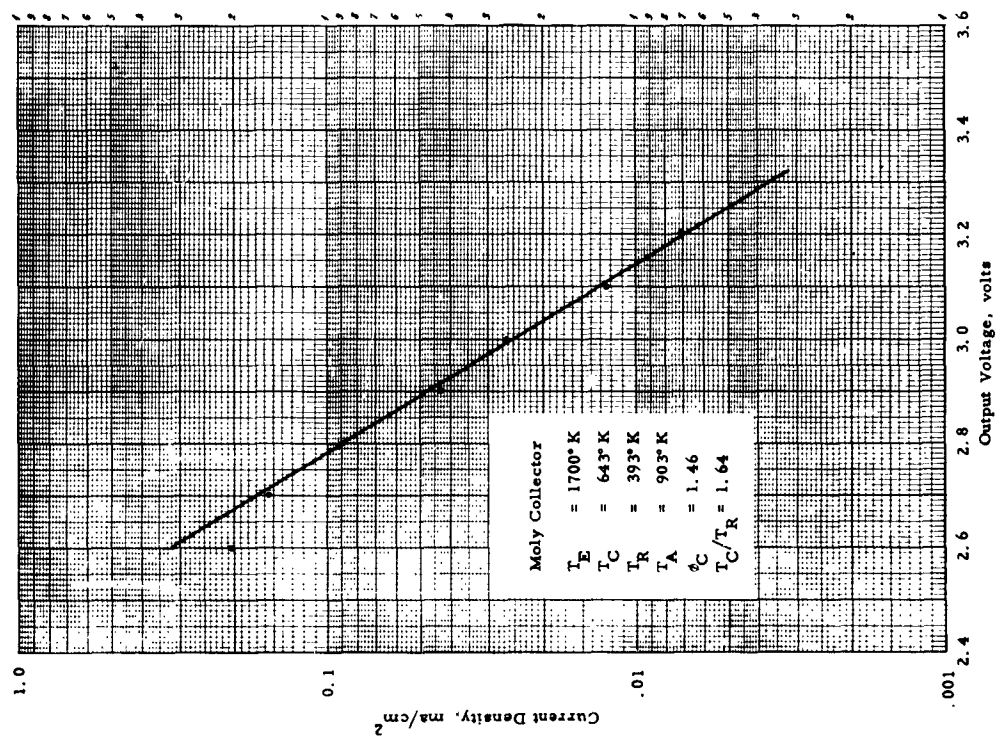


Figure IV-24 Semi-Log Plot

63-R-12-169

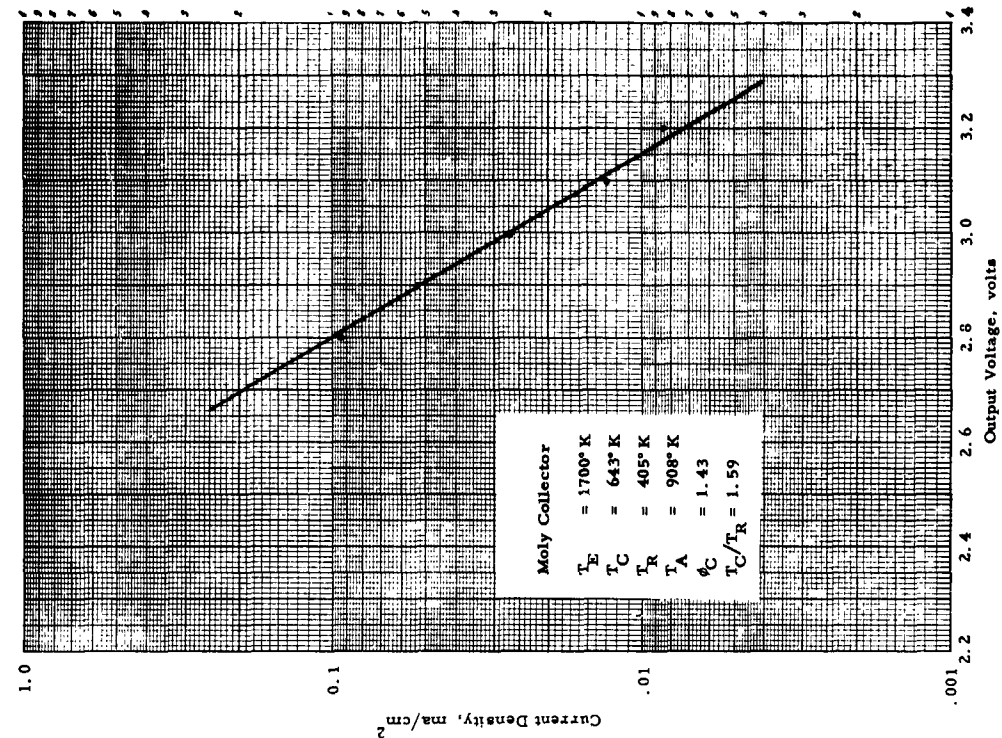


Figure IV-25 Semi-Log Plot

63-R-12-170

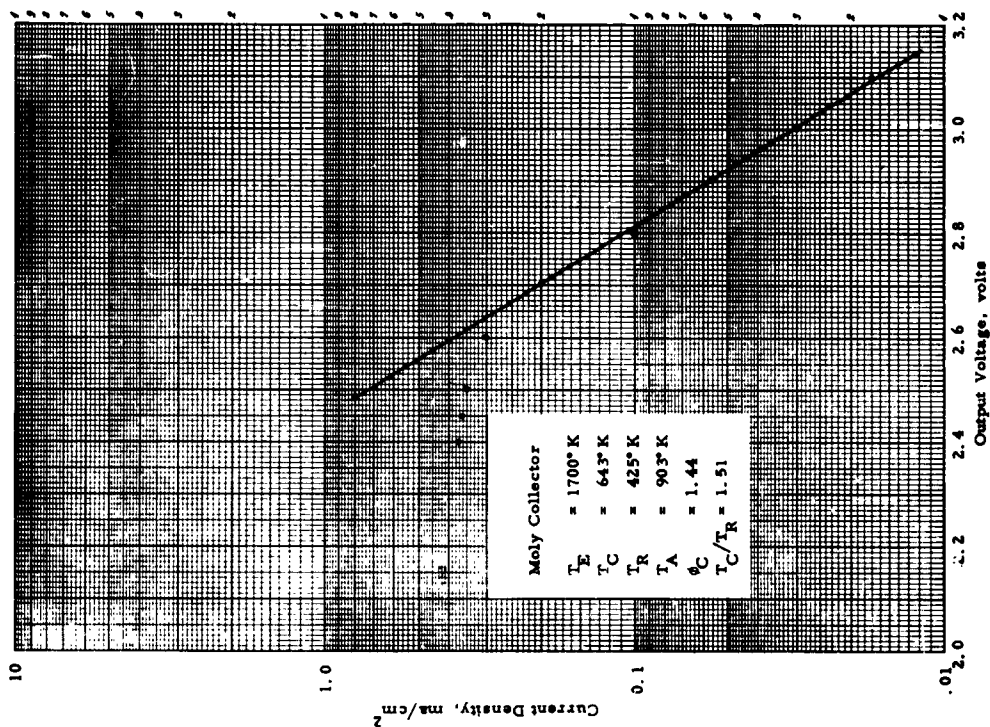


Figure IV-26 Semi-Log Plot

63-R-12-171

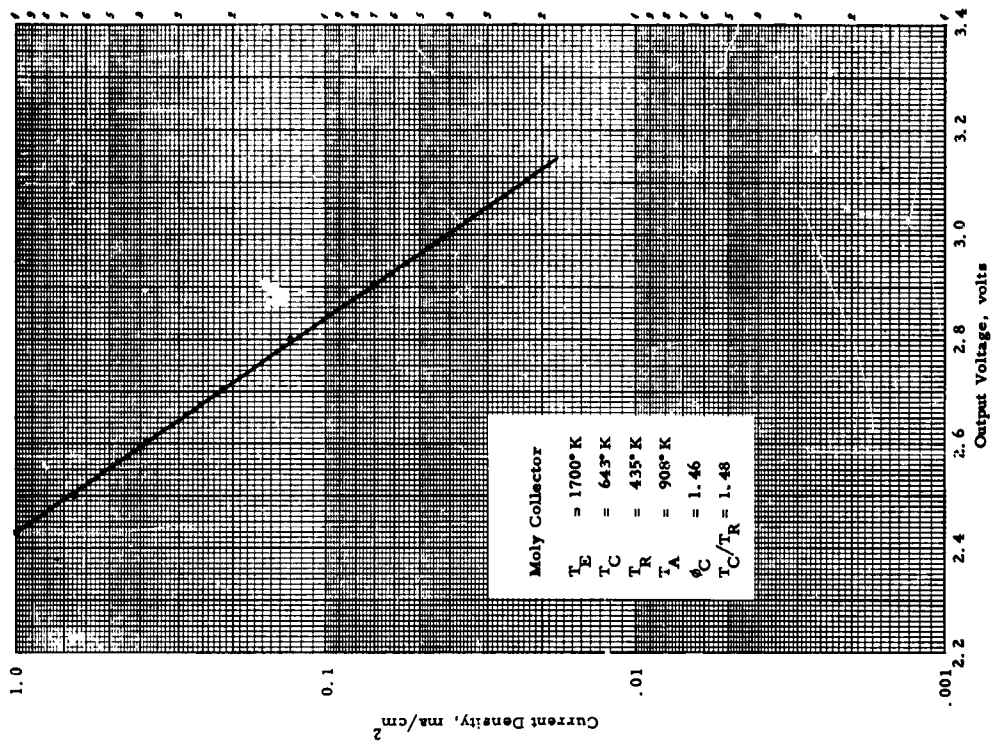


Figure IV-27 Semi-Log Plot

63-R-12-172

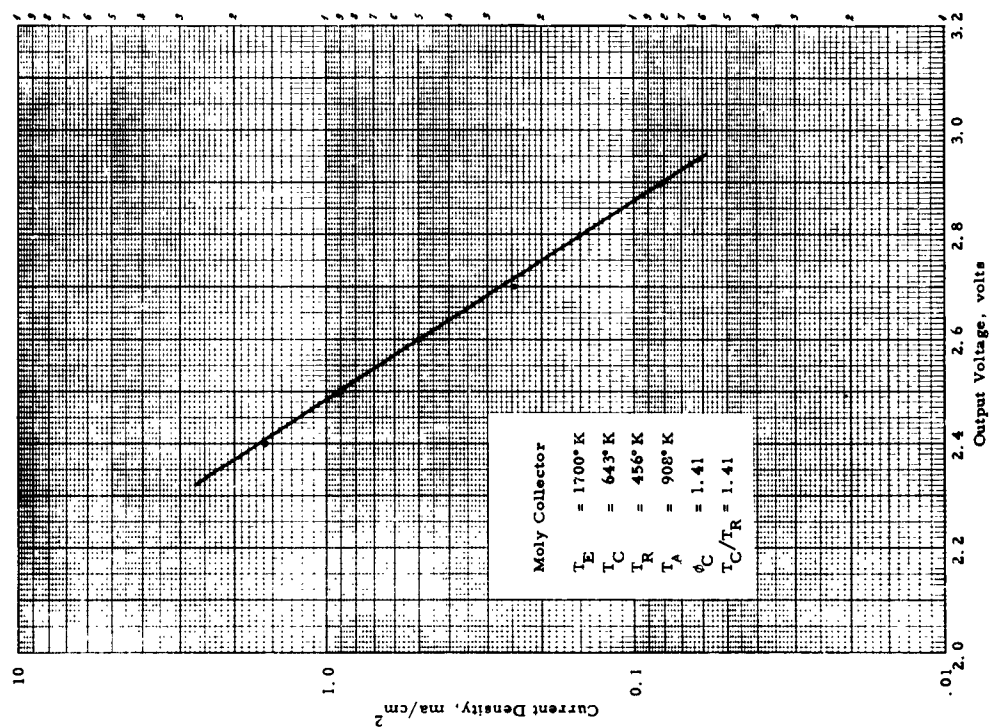


Figure IV-28 Semi-Log Plot

63-R-12-173

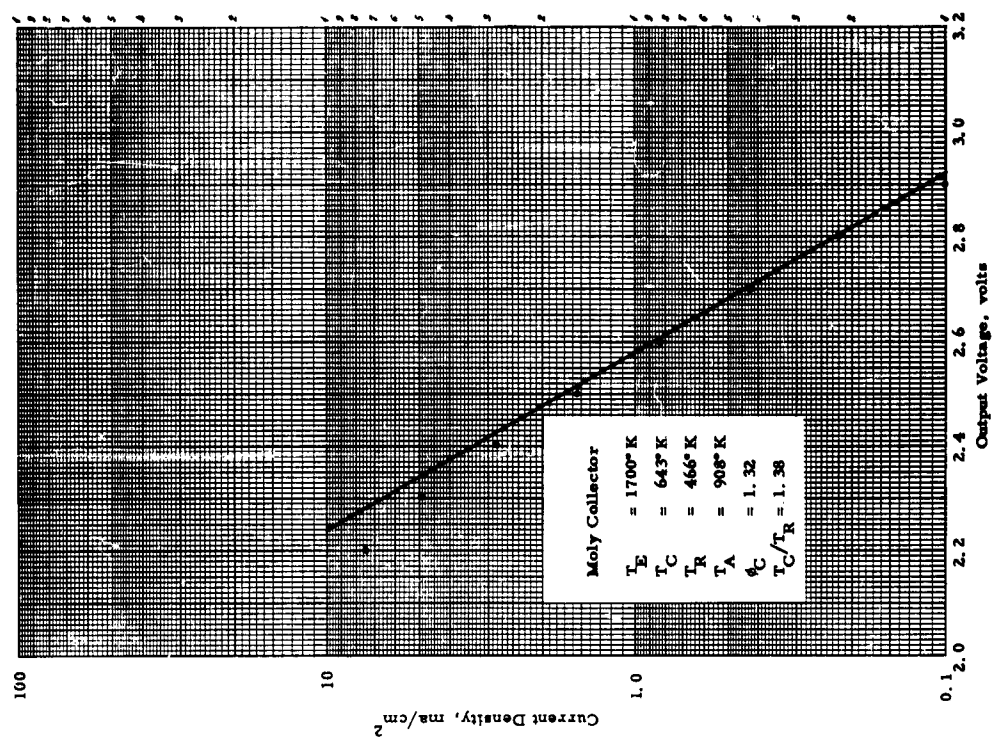


Figure IV-29 Semi-Log Plot

63-R-12-174

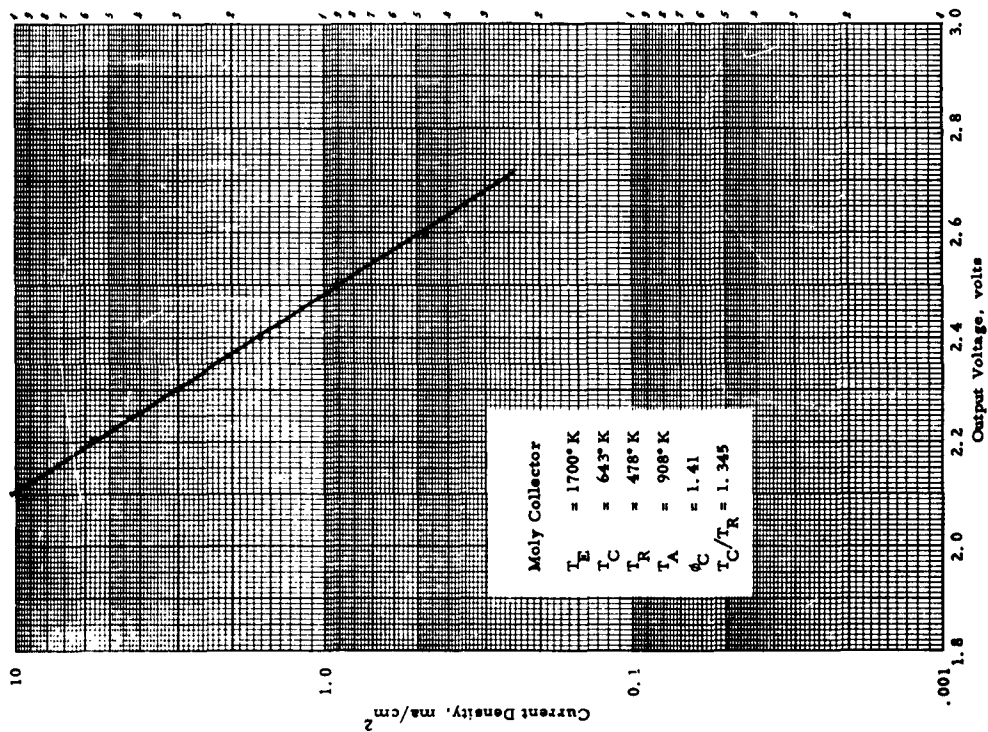


Figure IV-30 Semi-Log Plot

63-R-12-175

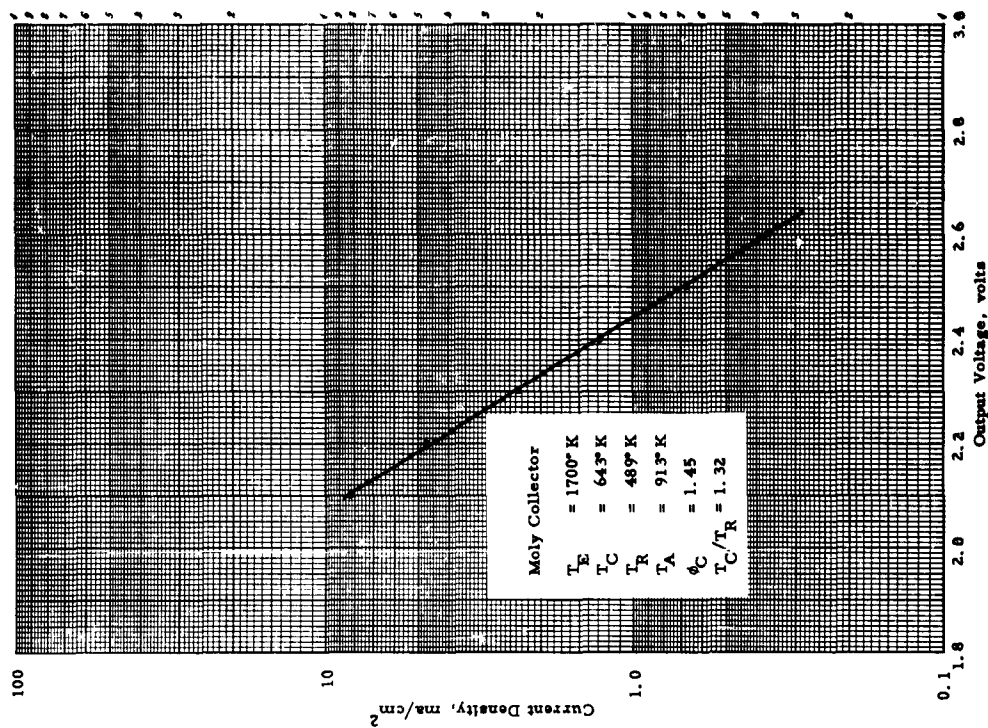


Figure IV-31 Semi-Log Plot

63-R-12-176

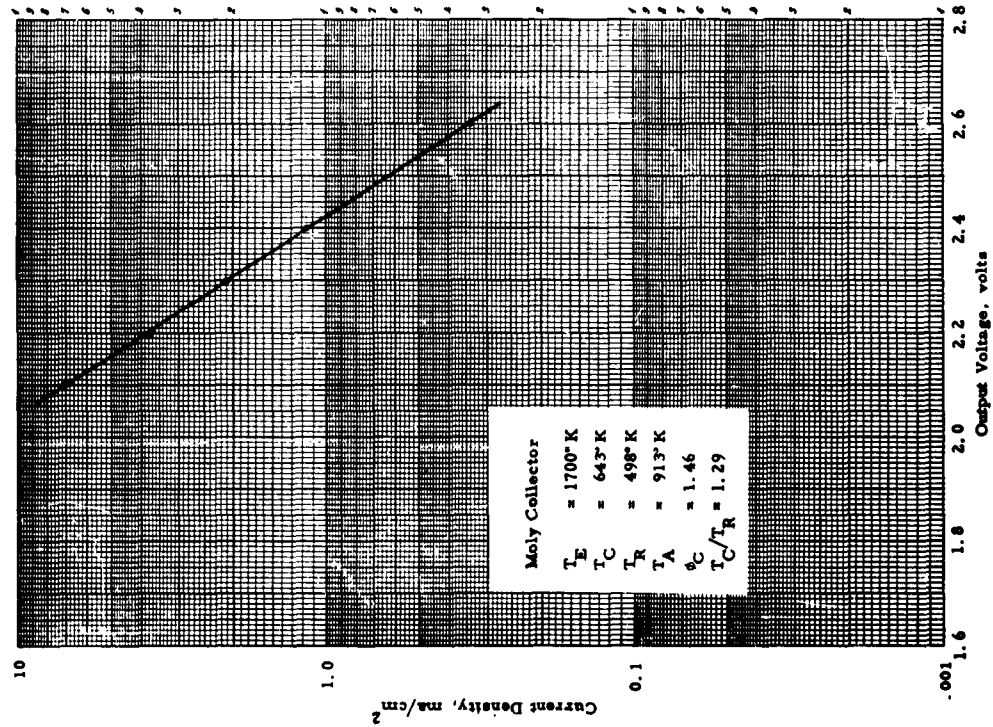


Figure IV-32 Semi-Log Plot

63-R-12-177

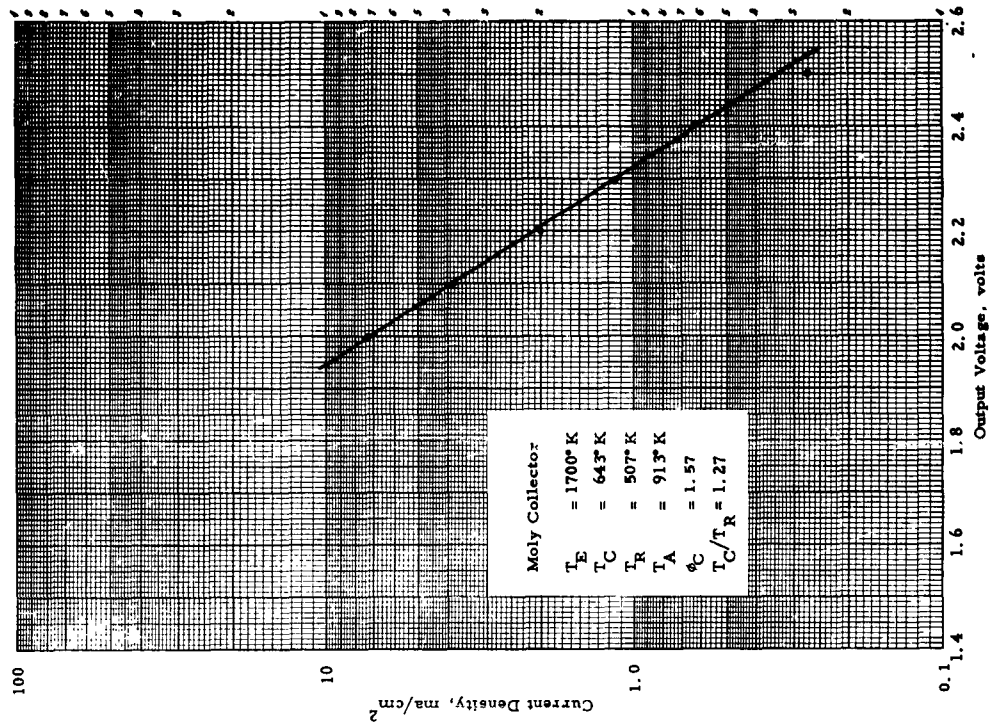


Figure IV-33 Semi-Log Plot

63-R-12-178

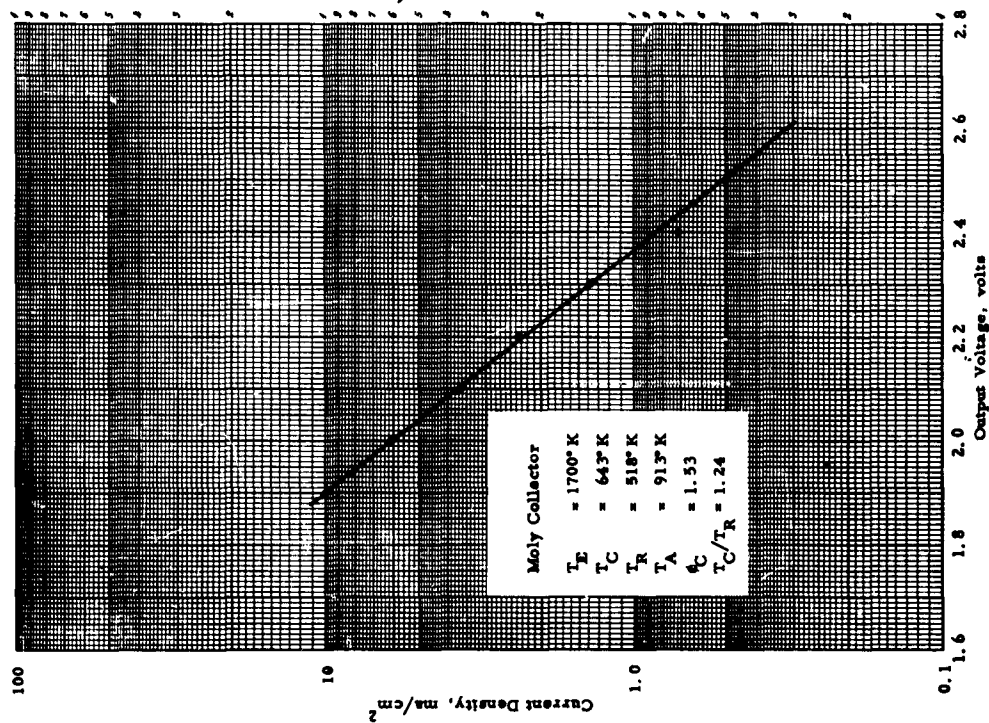


Figure IV-35 Semi-Log Plot

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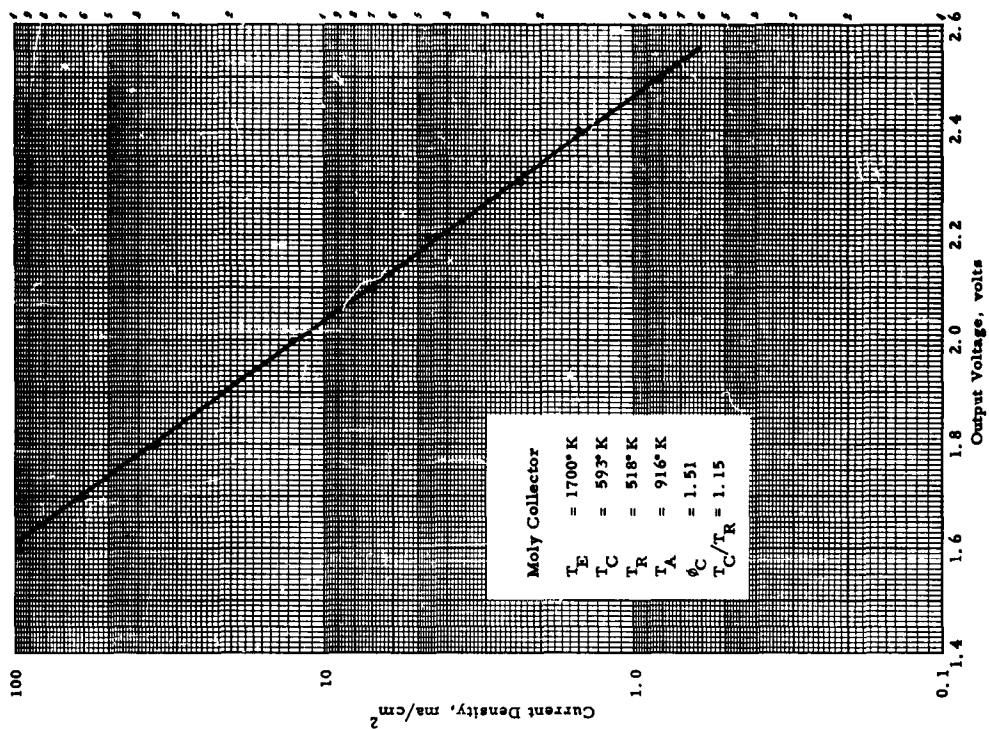


Figure IV-34 Semi-Log Plot

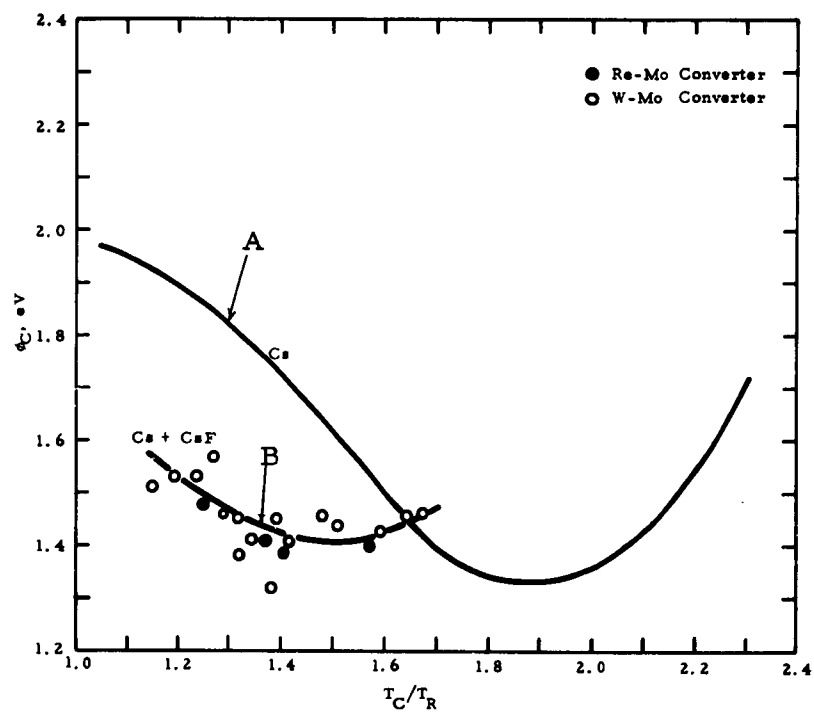


Figure IV-36 Collector Work Function Correlation Curves

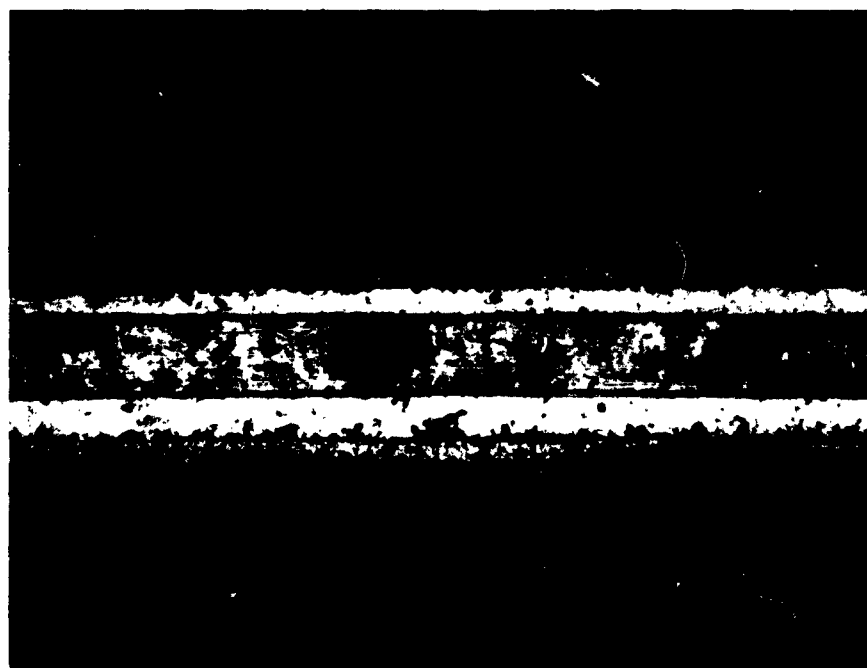


Figure IV-37 Metal-Ceramic Seal, Etched (75x)

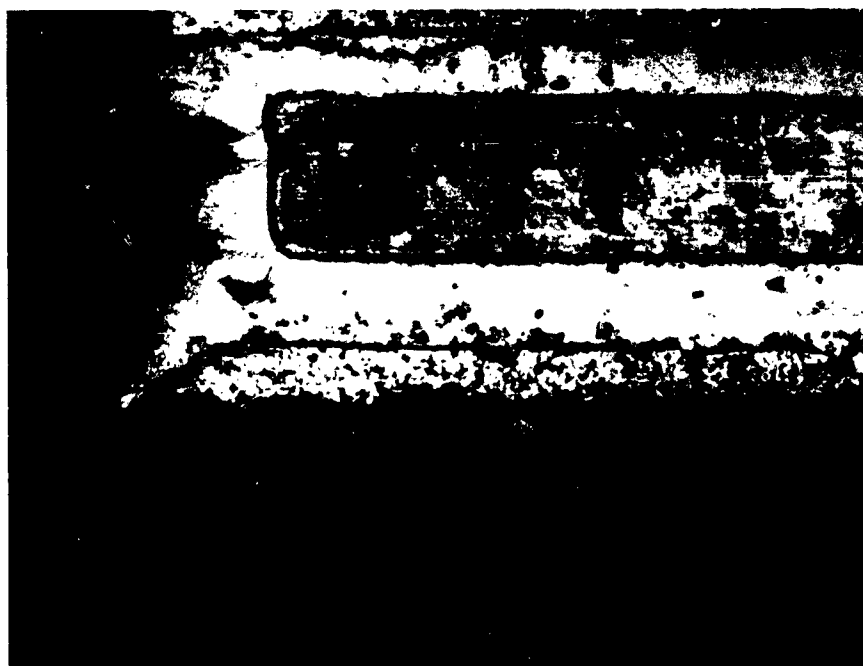


Figure IV-38 Metal-Ceramic Seal, End Exposed to Diode Atmosphere,
Etched, (150x)

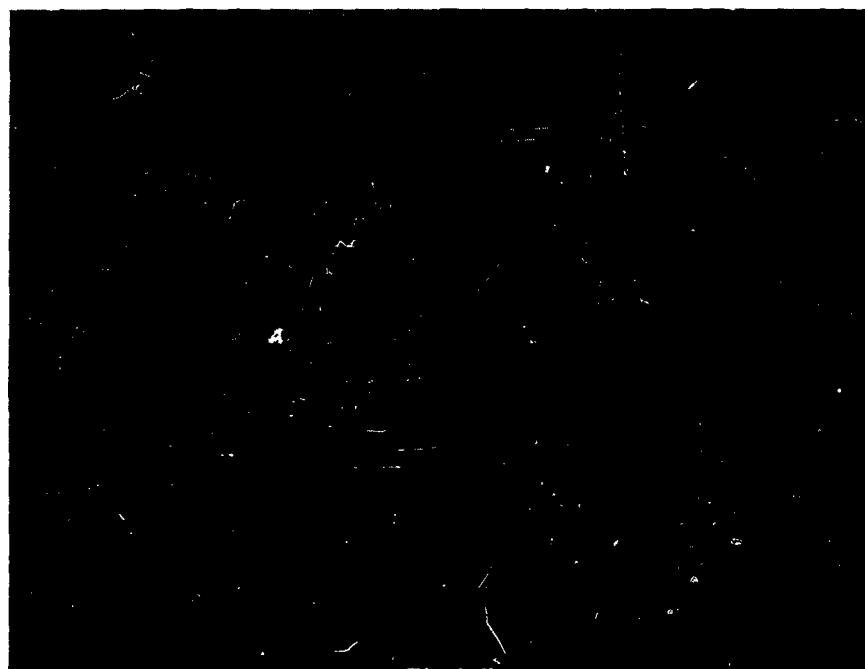


Figure IV-39

Cu-Ni Tubulation Braze, End of Fused Zone at Side of
Picture, Unetched, (560x)



Figure IV-40

Ni-Mo Tubulation Braze, Lightly Etched, Showing
Bevelled End of Ni Tube, (75x)

63-R-12-185

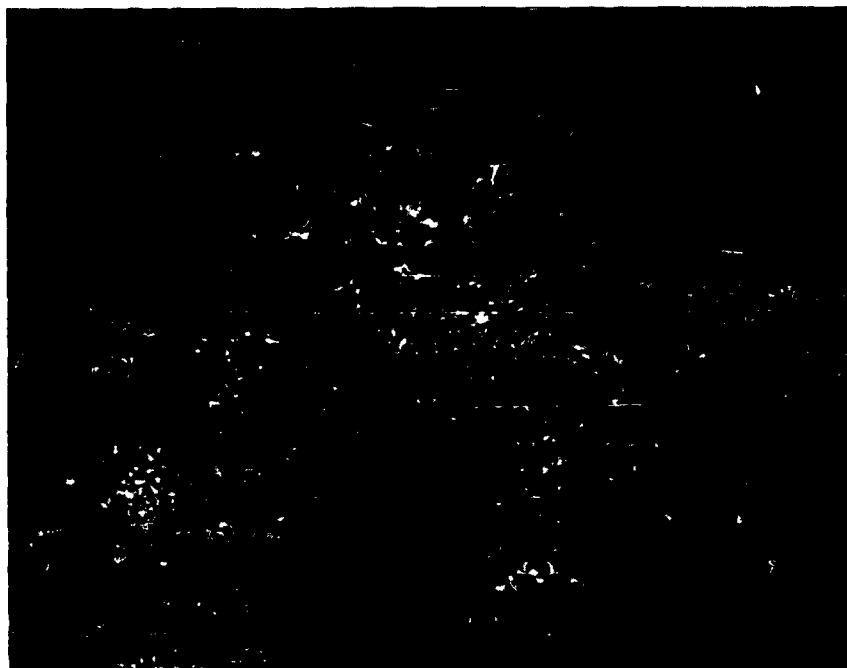


Figure IV-41 Inside of Ni Tube, (310x)



Figure IV-42 Inside of Cu Tube, (150x)

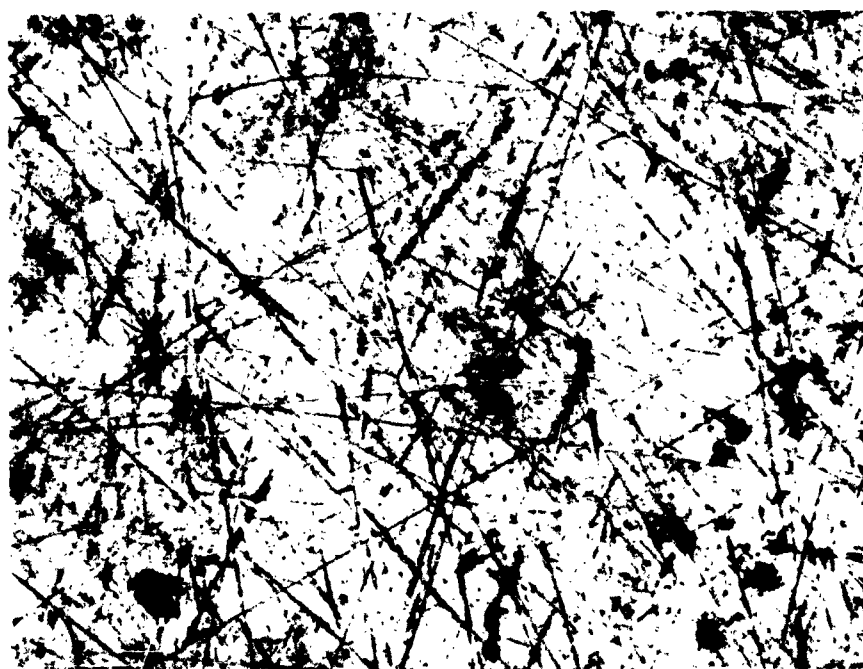


Figure IV-43 Collector Face after Swabbing with Water, (75x)



Figure IV-44 Mo-Ni Braze Exposed to Diode Atmosphere, Etched, (75x)

63-R-12-189



Figure IV-45 Ta-Mo Braze Exposed to Diode Atmosphere, Etched, (75x)

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

The experimental evidence presented clearly shows that the presence of cesium fluoride in cesium vapor thermionic converters results in an enhancement of the converter performance. This enhancement appears to be due wholly to a reduction of collector work function by approximately 0.1 volt. Measurements of collector work function in the presence of cesium fluoride have confirmed this conclusion. However, it should be pointed out that the value of the minimum collector work function has not been lowered. Rather, the curve which correlates collector work function to the ratio of collector and reservoir temperature T_C/T_R has been shifted toward lower values of T_C/T_R , which results in a closer approach to the minimum collector work function. Since the cesium reservoir temperature T_R is primarily dictated by emitter requirements, the only way previously available to approach this minimum was to increase the collector temperature T_R which resulted in a rapid decrease in output current due to collector emission. Thus, the addition of cesium fluoride has provided a new variable by which this previous constraint can be removed.

The fact that the converter performance is independent of the additive reservoir temperature, once a certain threshold is achieved, makes it possible to avoid the use of two reservoirs which may prove cumbersome in certain applications. The fluoride can be introduced in a region close to the collector which is at a temperature above the required threshold. An orifice has to be provided, however, at the beginning of the tubulation leading to the cesium reservoir. This orifice will greatly reduce the flow of additive into the colder cesium reservoir. A certain amount of fluoride will, of course, flow through this orifice but, due to its low vapor pressure, this amount will be extremely small and operating lives of many thousands of hours can be achieved by introducing a limited amount of fluoride at the collector base.

Cesium chloride has proved somewhat inferior to cesium fluoride in its ability to enhance converter performance. Moreover, there appears to be no other reason for preferring the chloride over the fluoride. Since the additive appears to achieve its beneficial effects on performance by lowering the collector work function, there appears to be no reason to believe that the same effects cannot be achieved with any emitter material, the only reservation being any possible corrosive effects on other emitter materials which were not tested in this program.

The work reported is regarded as the first step in the process of investigating the advantages offered by cesium halide additives to the conversion process. But as is frequently the case, the present investigation has posed new questions in the process of achieving its objective.

The initial time lag in the response of converter performance to the presence of the additive, as well as the insensitivity of performance to the additive reservoir temperature after a threshold temperature is reached, suggests that the additive adsorbed on the electrodes is not in equilibrium with the additive in the reservoir. Understanding the physics of this process will be a significant advance in surface physics but it will be equally valuable for optimizing the use of the additive to attain even greater gains in performance. For example, there is no obvious reason at this time why the work-function-vs- T_C/T_R curve cannot be shifted to even lower T_C/T_R values, making possible the utilization of even lower collector work functions.

To capitalize on the knowledge gained in the present program, as well as accelerate the use of halide additives in hardware devices, the following experimental work is recommended:

1. The effects of CsF alone in a research-type test vehicle should be investigated prior to the introduction of cesium. Such a test vehicle should have the

CsF reservoir located as close as possible to the interelectrode space. This investigation would make possible the determination of the relationship of electrode coverage to the reservoir conditions. The pressure of additive in the interelectrode space can be determined by measurement of positive and negative ion currents and compared with the pressure expected from vapor pressure data. Such measurements should be conducted under steady state and transient conditions.

2. The work up to now has indicated that the beneficial effects of the halides are taking place on the collector surface. The dependence of collector work function on additive pressure and on other variables should be more accurately defined than was possible in the present program. A test vehicle with an active collector guard ring should be employed, a scheme which removes most ambiguities from collector work function measurements, and greatly increases the accuracy of the experiment. Particular attention should be paid to the dependence of the ϕ vs T_C/T_R correlation to the additive pressure, again under steady state and transient conditions.

3. The ultimate users of additives will, of course, be the hardware designers. To them the use of a second reservoir, the temperature of which has to be controlled, is an undesirable complication. The results up to now, which indicate that a second reservoir will not be necessary, are therefore encouraging. However, the single reservoir concept for hardware designs must be developed and tested experimentally, before being turned over to the hardware designers for use in power generator programs.

REFERENCES

1. I. Langmuir, D. S. Villars, "Oxygen Films on Tungsten", JACS 53, 486 (1931).
2. R. L. Aamodt, L. J. Brown, and B. D. Nichols, "Thermionic Emission from Molybdenum in Vapors of Cesium and Cesium Fluoride", Power Information Center Conference, December 6 and 7, 1961.
3. "Electron Emission of Tungsten in a Cesium Fluoride Atmosphere", AIAA Conference Paper, Paris, France, August 1963.

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